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To the Graduate Council:

I am submitting herewith a dissertation written by Huan Chen entitled "Potential Emissions and Exposures of Toxic Organics from Storage Tanks for Chemical Additions in Hydraulic Fracturing: A Modeling Approach." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Civil Engineering.

Kimberly E. Carter, Major Professor

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Joshua S. Fu, Qiang He, Paul D. Terry, Wenjun Zhou

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Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Potential Emissions and Exposures of Toxic Organics from Storage Tanks for Chemical Additions in Hydraulic Fracturing: A Modeling Approach

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Huan Chen

December 2016

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DEDICATION

This dissertation is dedicated to my advisor (Dr. Kimberly E. Carter), my committee members (Dr. Joshua S. Fu, Dr. Qiang He, Dr. Paul D. Terry, and Dr. Wenjun Zhou), and my family (Qilin Chen, Ming'e Zhang, and Jianxiong Chen).

ACKNOWLEDGEMENTS

The moonlight is sprinkling on the window, and I am sitting in my apartment to write the part of acknowledgements in the dissertation, which is for my Ph.D. degree from the University of Tennessee, Knoxville, a university in the United States (U.S.). Time flies, and I cannot remember how many nights I spent and how many weekends it costs me to arrive at this final step. I guess I cannot make it without my industrious and assiduous attempts, and moreover without all merciful and graceful favors from the surrounding people. Thanks to my parents and my younger sister, they helped me making the tough decision of resigning my job and coming here for the Ph.D. degree which I had dreamed for several years. Acknowledgements to my advisor - Dr. Kimberly E. Carter, for the opportunity she offered to work together with her three years ago and for her continuously advising on my research during those three years. If I have any improvements on my academic career, it is because of her enduring training and cultivations. Thanks to my group members, Laura W. Matzek and Katherine E. Manz, for their company which makes me feeling I am not the only one who was suffering and struggling with the academic research and dissertation. Thanks to my friends living in the U.S. and China, their comforts and encouragements are the oases, without which I cannot survive when going through the desert. Thanks to my committee members (Dr. Joshua S. Fu, Dr. Qiang He, Dr. Paul D. Terry, and Dr. Wenjun Zhou), for willingly serving on my committee and providing the critical reviews and suggestions which improve my dissertation significantly. I am deeply aware that I cannot enjoy my academic life in the palace of science and engineering without their assistances. Hope all of them having a good and enjoyable life.

Huan Chen

June 3, 2016

Knoxville, TN

ABSTRACT

Hydraulic fracturing has promoted the exploitation of natural gas in the United States (U.S.). However, the storing and emptying of chemical additives in hydraulic fracturing wells may pose adverse effects through inhalation exposures. Based on the information about hydraulic fracturing fluids, this study investigated: 1) water volumes used to mix chemical additives for making up the hydraulic fracturing fluids; 2) chemical species, concentrations and their degradability in the hydraulic fracturing fluids; 3) emissions of organics from chemical storage tanks; and 4) the occupational inhalation exposures by toxic and organic vapors.

Results shows for 80,047 wells fractured between 2008 and 2014 and located in the 14 states studied, the highest total amount of water was consumed in Texas with 457.42 Mm^3 of water used to fracture 40,521 wells; followed by Pennsylvania with 108.67 Mm^3 of water used to treat 5,127 wells. For 5,071 wells completed in 2008 through July 2014 and located in the Marcellus Shale Formation, there were totally 517 chemicals introduced into the hydraulic fracturing fluids. Although most of the added chemicals can be removed with the appropriate treatments, the degradation of some chemicals would produce more toxic and persistent degradation produces.

For 72,023 out of 80,047 wells, the median daily emission values were 0.221 kg d^{-1} per well. Those emissions were primarily contributed by the non-methane volatile organic compounds (NMVOCs). Furthermore, 95.14% of emissions caused by all NMVOCs were due to 60 NMVOCs which belong to the 847 candidate substances for the Priority List of Hazardous Substances defined by Agency for Toxic Substances & Disease Registry (ATSDR) in 2011. Results shows there were 2,893, 8, 4,415, and 2,992 out of 60,644 wells with the possibilities of the acute exposure for non-cancer risks, the chronic exposure for non-cancer risks, the acute exposure for cancer risks, and the chronic exposure for cancer risks on workers. Methanol was the major organic causing the acute exposure for non-cancer risks in hydraulic fracturing. Formaldehyde was the dominant contributor to both the acute and chronic exposures for cancer risks.

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CHAPTER 1

INTRODUCTION

1.1. Background

Due to the advance in hydraulic fracturing and horizontal drilling technologies, shale gas production has increased greatly in the United States (U.S.) in the past several years (Struchtemeyer et al., 2012; Zhou et al., 2014b). U.S. Energy Information Administration (2011) reported there are between 134.75 billion and 750 trillion cubic feet of recoverable shale gas and oil in the U.S. As shown in Figure 1-1, the monthly dry shale gas production increased from 2.15 million cubic feet per day in 2000 to 84.33 million cubic feet per day in 2015 (U.S. Energy Information Administration, 2015). In 2010, 23% of the total U.S. dry gas production was shale gas, and this percentage will increase to 49% in 2035 (Jiang et al., 2014). With the fast development of shale gas, the undesirable environmental and health impacts of this technology have already attracted public attention (Arthur et al., 2009; Gregory et al., 2011; Jain, 2015).

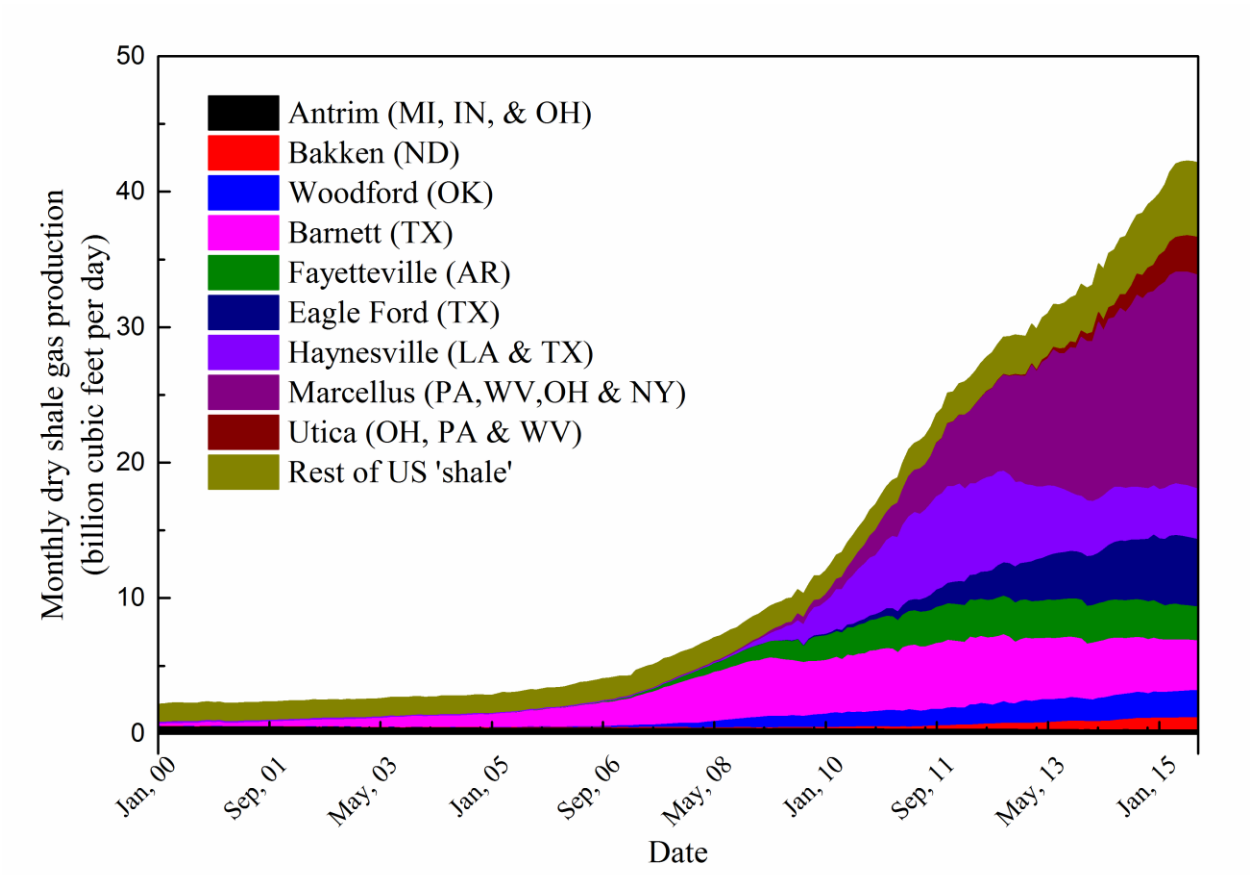

Figure 1-1. Monthly dry gas production in shale plays from January 2000 to January 2015 (U.S. Energy Information Administration, 2015).

Hydraulic fracturing is a stimulation technology that pumps large volumes of hydraulic fracturing fluids into the shale formations, to create fractures and openings for shale gas recovery (Struchtemeyer and Elshahed, 2012b; Struchtemeyer et al., 2012; Obo, 2013; Kim and Moridis, 2015). The long horizontal laterals drilled by using horizontal drilling increases the contact area between formations and hydraulic fracturing fluids. The large volumes of water used in hydraulic fracturing is related to the vertical depth of the wells and is dependent on the shale plays, operators, the lateral lengths, and the number of "fracking" stages (Nicot and Scanlon, 2012).

The amount of water used was determined for different shale plays throughout the United States. The estimated water use for Barnett was 145 Mm^3 (3.83×10^{10} US gal) for around 15,000 wells between 2000 to mid-2011 (Nicot and Scanlon, 2012), and 210 Mm^3 (5.55×10^{10} US gal) between 1981 and 2012 (Nicot et al., 2014). Scanlon et al. (2014a) reported the cumulative amount of water used were ~150 Mm^3 for 8,301 wells in the Eagle Ford Shale Play (2009-2013), and 5.8×10^9 gal (~59.81 Mm^3) for 7,868 wells in the Bakken (2005-2013). The large amounts of water needed for hydraulic fracturing may also contribute to drinking water or groundwater contaminations due to inappropriate managements (Llewellyn et al., 2015). These concerns are more critical for the shale plays located in areas where water scarcity is known to occur (Kargbo et al., 2010; Nicot and Scanlon, 2012). However, studies on the water usage have been focused on the shale plays and there few reports if any have been concerned with the overall water usage for hydraulic fracturing in the U.S. In most of the studies, there also have been discrepencies regarding the amount of water used and also returns after fracturing. According to Vengosh et al. (2014), the estimated volumes of wastewater per shale gas well were 3,500 m^3 in Marcellus Shale, Pennsylvania (2012), and 4,000 m^3 in Niobrara, Colorado (2012); however, Stringfellow et al. (2014) estimated the volume of flowback per well to be between 1,900-9,000 m^3.

Water management strategies are still being investigated because of the large volumes of water being used and return to the surface as wastewater. Recycling or reusing the water from hydraulic fracturing is considered to be a management strategy for oil and gas operations (Warner et al., 2013; Mauter and Palmer, 2014). Recycling oil and gas wastewater can reduce, not only water consumption in hydraulic fracturing

(Gregory et al., 2011), but also the amount of water transported to wastewater treatment plants (WWTPs) or injected into Class II deep wells. Compared with other applications (e.g. irrigation), wastewater can reach the requirements set for recycling into hydraulic fracturing after relatively simple treatments (Lester et al., 2015a). Increasing the amount of brackish groundwater and produced water used can alleviate the limitations on the future development of shale gas and oil production (Scanlon et al. (2014b), while decreasing the amount of freshwater usage. However, the volume of recycled wastewater in hydraulic fracturing fluids is unclear and needs to be disclosed.

Hydraulic fracturing fluid are not only composed of ~99.5% water and proppants but also includes approximately 0.5% chemical additives (Arthur et al., 2009; Gregory et al., 2011). The chemical additives employed in hydraulic fracturing fluids are used as friction reducers, surfactants, scale inhibitors, biocides, and corrosion inhibitors (Arthur et al., 2009; Gregory et al., 2011; Aminto and Olson, 2012). Of all the chemicals used, it was discovered that there were 13 different carcinogens contained in 95 products used by the hydraulic fracturing operators (U.S. House of Representatives, 2011). Stringfellow et al. (2014) identified 81 common chemicals existing in the hydraulic fracturing fluids. Of these chemicals 5 were confirmed or suspected carcinogens, including ethanol, naphthalene, diethanolamine, acetaldehyde, and thiourea. Information about the chemical species added in hydraulic fracturing fluids provides limited support for risk management as well as wastewater treatment. Important information, such as the number of wells in which the toxic chemicals were added, their frequency and concentrations in hydraulic fracturing fluids, is lacking.Hydraulic fracturing fluids pose a health risk because of the toxic chemicals used to make up these fluids (Wattenberg et al., 2015).

Potential exposures and health effects from hydraulic fracturing have been well reviewed by the previous studies (Adgate et al., 2014; Shonkoff et al., 2014; Werner et al., 2015). Shonkoff et al. (2014) evaluated the environmental health impacts due to the developments of shale gas. The deteriorations in the air and water qualities were considered as the major environmental impacts, and the potential exposures caused by the operations on hydraulic fracturing fluids were highlighted. Similarly, Werner et al. (2015) suggested water, air, noise, light, and traffic were the major environmental medias which would be affected

by hydraulic fracturing and pose the potential health effects on the workers and residents living around the hydraulic fracturing areas. Adgate et al. (2014) described the possible exposure pathways and health effects associated with unconventional natural gas production. The on-site emission sources put the workers at the exposure of air pollutions, and moreover the incidents, malfunctions, and traffic accidents would increase their health exposures. The chemicals used in the hydraulic fracturing have the possibility to contaminate the drinking water sources and thus have the health risks on the residents through the ingestion exposures. Ingestion, skin contact, and inhalation are considered as the general routes leading to health exposures by U.S. EPA (2011). The hydraulic fracturing wells have the possibility to posed the health effects on the workers through the inhalation exposure to the air pollutions and the skin-contact exposure to the fluids with toxic chemicals. Besides the inhalation exposure to the air pollutions, the residents have the potential to be exposure to the contaminated drinking water through the ingestion. The major exposure pathways due to the activity of hydraulic fracturing are shown in Figure 1-2.

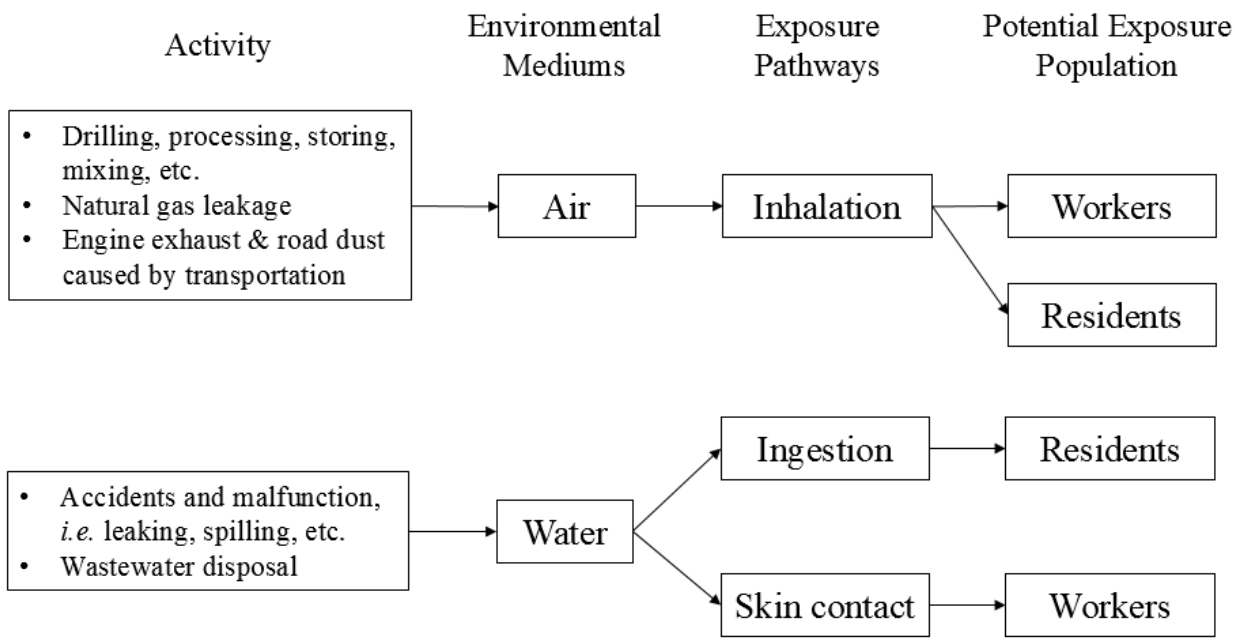

Figure 1-2 Evaluation of the major exposure pathways caused by the hydraulic fracturing.

Figure 1-3. A truck transporting the white plastic intermediate bulk containers filled with the chemical additives to a hydraulic fracturing well (McFeeley M., 2012). Source: McFeeley M. (2012). "State Hydraulic Fracturing Disclosure Rules and Enforcement: A Comparison." IB: 12-06-A. Retrieved Dec 18, 2015, from https://www.nrdc.org/sites/default/files/Fracking-Disclosure-IB.pdf.

There are a number of ways for human exposure to hydraulic fracturing fluids, such as leaks, spills, as well as release from storage tanks (Shonkoff et al., 2014). Stringfellow et al. (2014) found 12 organics in the hydraulic fracturing fluids were non-methane volatile organic compounds (NMVOCs) or semi-volatile organic compounds (SVOCs). After reviewing their inhalation toxicity in literature, they suggested the inhalation exposure cannot be overlooked and should be further investigated. NMVOCs and SVOCs can be evaporated from the liquid and introduced to the air. The toxic vapors will cause adverse health affects via inhalation exposure (Zhou et al., 2011). For example, 2-butoxyethanol, which is used as foaming agent in hydraulic fracturing fluids (Stringfellow et al., 2014), is capable of causing irritant effects through inhalation and dermal exposures (Bello and Quinn, 2013). Until now, there was no attention on potential inhaled risks of chemical additives prior to the addition of these chemicals to hydraulic fracturing fluids. Vapor recovery systems (*i.e.* Stage I and Stage II in gasoline vapor recovery) can greatly reduce the emissions from liquid to air (Saarinen et al., 2000; Cruz-Nunez et al., 2003), however this system has not been adopted in chemical storage tanks in hydraulic fracturing (Figure 1-3). The storing and emptying of chemical additives stored in hydraulic fracturing wells would cause the evaporation of NMVOCs and SVOCs to the atmosphere, which can have passive effects on human health, especially for workers around the wells. For the purpose of estimating inhalation exposure associated with storing and emptying operations on chemical additives, the emissions data from these chemicals is necessary.

1.2. Objectives, Hypothesis and Studies

The overall objective in this dissertation is to investigate the potential for occupational exposures to toxic vapors from chemical storage tanks. The null hypothesis (H_0) is that without the installation of vapor recovery and treatment systems, the storing and emptying operations on chemical storage tanks will not leak potentially harmful levels of chemicals. In order to test this null hypothesis, four studies were carried out in this dissertation and the schematic diagram about those studies are shown in Figure 1-4.

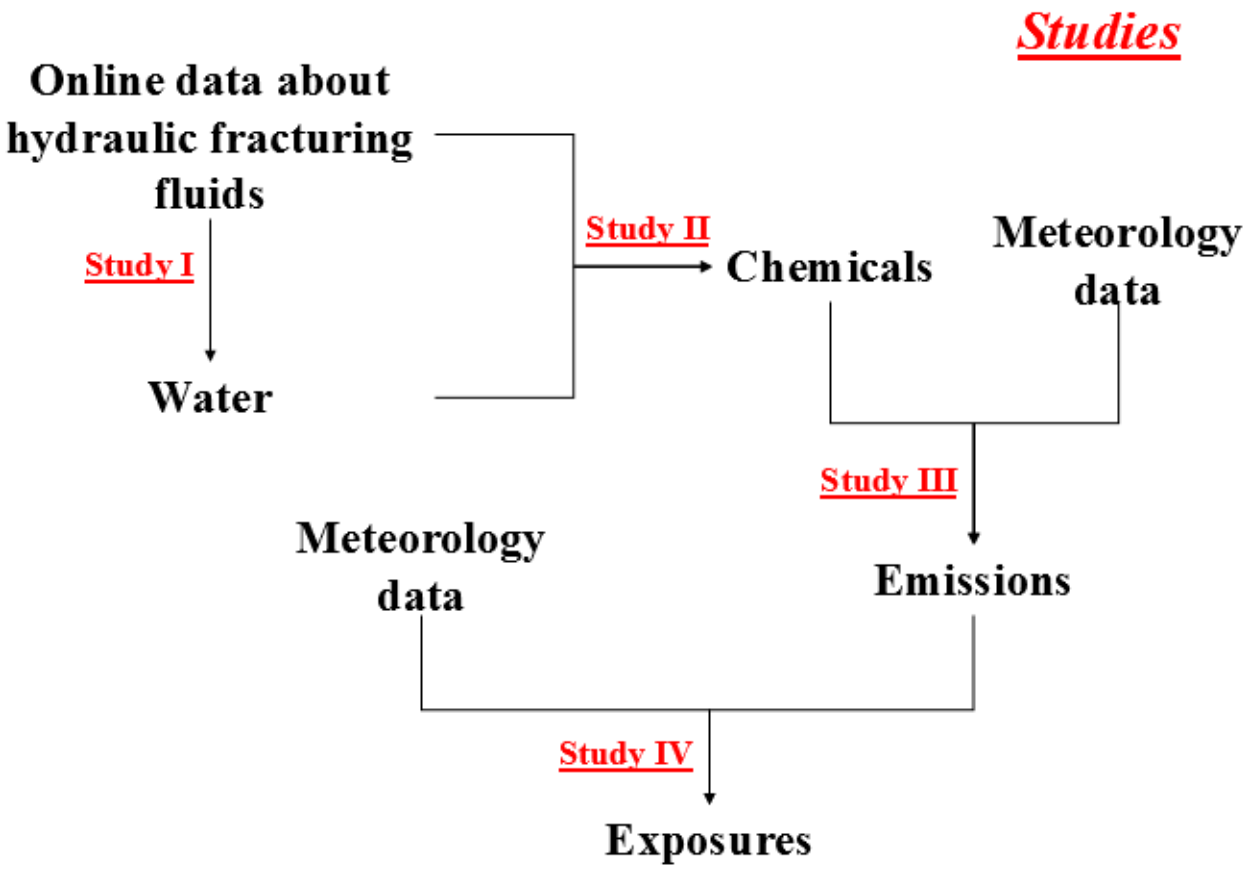

Figure 1-4. Schematic diagram about four studies carried out in this dissertation

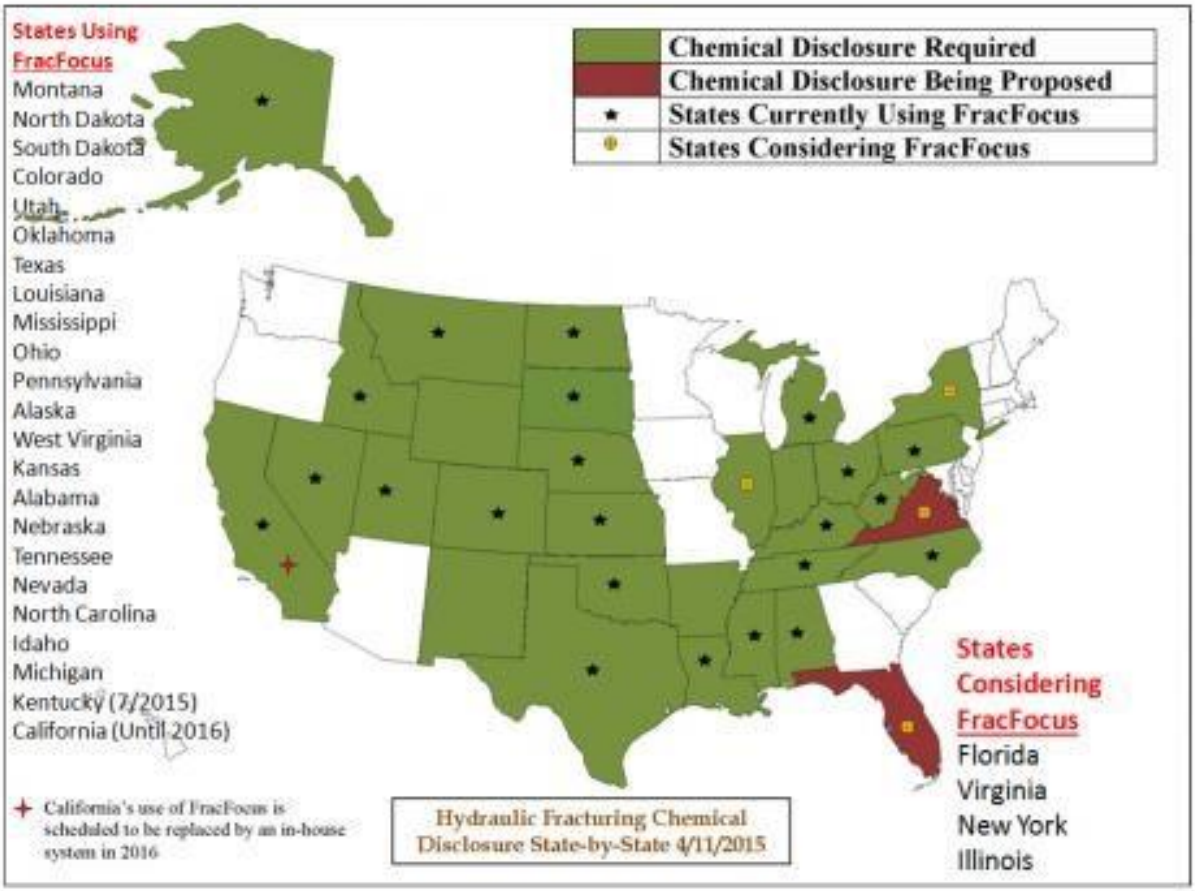

Figure 1-5. U.S. States using FracFocus. Source: https://fracfocus.org/welcome. Accessed on 10/05/2015.

Study I in the Chapter 2

The objectives in the study I are: 1) to investigate the volume of water used in hydraulic fracturing and the vertical depth of hydraulic fracturing wells in recent years, as well as, 2) to evaluate the use of recycled produced water by the oil and gas industry. The hypotheses in the study I are: 1) the large water usage in hydraulic fracturing may enhance water scarcity and thus putting more strain on the water demands in certain areas of the United States, and 2) recycling wastewater in hydraulic fracturing which is a beneficial wastewater management may be broadly adopted.

Study II in the Chapter 3

The objectives in the study II are: 1) to investigate the types of chemicals added in hydraulic fracturing fluids (*i.e.* chemical species, the number of wells added a specific chemical and its frequency, average concentrations) in wells located in West Virginia and Pennsylvania, as well as, 2) to further analysis the toxicity and degradability of the introduced organic compounds. The hypotheses in the study II are: 1) toxic and even carcinogenic organics may be added into the hydraulic fracturing fluids, 2) some of the introduced organic compounds may be persistent in the aqueous phase, and 3) the toxic and persistent organics may be removed from the wastewater in the oil and gas industry when adopting the appropriate treatments.

Study III in the Chapter 4

The objectives in the study III are: 1) to investigate the emissions of wells and organics, especially NMVOCs and toxic and even carcinogenic organics, by using the Chapter 7 in AP-42 to estimate the amounts of organics emitted from chemical additives stored in fixed-roof liquid storage tanks in hydraulic fracturing wells. The model sensitivity and uncertainty analysis were carried out in order to understand the model better and estimate the biases. The hypothesis in the study III is that organic emissions from chemical storage tanks maybe important for considerations due to their quantity and toxicity.

Study IV in the Chapter 5

The objectives in the study IV are: 1) to investigate the spatial and temporal distributions of organic air concentrations around the hydraulic fracturing wells by using the AERMOND dispersion model, and 2) to estimate the possibility of the non-carcinogenic and carcinogenic exposure risks to the workers through

the inhalation exposure. The hypothesis in the study IV is that toxic vapors from chemical storage tanks may have the possibility to cause the health consequences.

1.3. Data Source

In order to perform health exposure assessment of toxic vapors from storage tanks for chemical additives, the information about chemical additives, such as their volumes and concentrations, is required. FracFocus online system (www.fracfocus.org) provides the information about the hydraulic fracturing wells (*i.e.* locations, fracturing date, water usage, vertical depth, and operators) and chemicals in their hydraulic fracturing fluids (*i.e.* chemical species, their concentrations in hydraulic fracturing fluids). The information for the chemical additives before being blended with fresh water to make up hydraulic fracturing fluids can be calculated from the information provided by FracFocus (water used in hydraulic fracturing fluids, water percentages in hydraulic fracturing fluids, and chemical percentages in hydraulic fracturing fluids). Therefore, the hydraulic fracturing data was collected from FracFocus online system.

The Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCCC) developed FracFocus Chemical Disclosure Registry. It is a publicly accessible online system and provides information about the hydraulic fracturing wells and the chemicals added in to the well's hydraulic fracturing fluids. A number of states throughout the U.S. require the oil and gas operators to disclose the information about the chemical additives used the in the hydraulic fracturing fluids on FracFocus (Figure 1-5). Processing FracFocus data provides the opportunities to investigate the chemicals and their associated risks, and also aid the chemical risk management for operators and related companies (Arthur et al., 2014). Although the significant information is available on the open site of FracFocus, until now there were few studies regarding the scrutinizing the data (Vengosh et al., 2014).

CHAPTER 2

WATER USAGE FOR NATURAL GAS PRODUCTION THROUGH HYDRAULIC FRACTURING IN THE UNITED STATES FROM 2008 TO 2014

A version of this chapter was originally published:

Chen, H. and K. E. Carter (2016). "Water usage for natural gas production through hydraulic fracturing in the United States from 2008 to 2014." Journal of Environmental Management **170**: 152-159.

Highlights

- From 2008 to 2014, 930 Mm^3 (2.46x1011 US gal) of water were used to fracture 80,047 wells.
- The percentage of water used for hydraulic fracturing in each state was lower than the water usages for other industries.
- The percentage of wells where recycled wastewater was used was lower in most states, except in Ohio and Arkansas.

2.1. Abstract

Hydraulic fracturing has promoted the exploitation of shale oil and natural gas in the United States (U.S.). However, the large amounts of water used in hydraulic fracturing may constrain oil and natural gas production in the shale plays. This study surveyed the amounts of freshwater and recycled produced water used to fracture wells from 2008 to 2014 in Arkansas, California, Colorado, Kansas, Louisiana, Montana, North Dakota, New Mexico, Ohio, Oklahoma, Pennsylvania, Texas, West Virginia, and Wyoming. Results showed that the annual average water volumes used per well in most of these states ranged between 1,000 m3 and 30,000 m3. The highest total amount of water was consumed in Texas with 457.42 Mm3 of water used to fracture 40,521 wells; followed by Pennsylvania with 108.67 Mm3 of water used to treat 5,127 wells. Water usages ranged from 96.85 Mm3 to 166.10 Mm3 annually in Texas from 2012 to 2014 with more than 10,000 wells fractured during that time. The percentage of water used for hydraulic fracturing in each state was relatively low compared to water usages for other industries. From 2009 to 2014, 6.55% (median) of the water volume used in hydraulic fracturing contained recycled produced water or recycled hydraulic fracturing wastewater. 10.84% (median) of wells produced by hydraulic fracturing were treated with recycled produced water. The percentage of wells where recycled wastewater was used was lower, except in Ohio and Arkansas, where more than half of the wells were fractured using recycled produced

water. The median recycled wastewater volume in produced wells was 7,127 m3 per well, more than half the median value in annual water used per well 11,259 m3. This indicates that, for wells recycling wastewater, more than half of their water use consisted from recycled wastewater.

2.2. Introduction

2.2.1. Background

Hydraulic fracturing is used to create fractures in shale formation and has become common practice over the last several years for the production of natural gas in the United States (U.S.). The production of natural gas, especially in various low-permeability shale plays, has increased from 2008 to 2014 due to the use of hydraulic fracturing and horizontal drilling techniques (Jiang et al., 2011; Sakmar, 2011; Vengosh et al., 2014). However, the practice of hydraulic fracturing concerns many environmental groups, policy makers, and scientists due to the potential risks to the environment and human health. Hydraulic fracturing consists of large volumes of hydraulic fracturing fluids, which consist of a mixture of 98 to 99.5 % water, proppants, and chemical additives making up the balance (Gregory et al., 2011), being injected into the shale formation under high pressure. Roughly 30-50% of the injected water flows back to the surface after the pressure is released (Stringfellow et al., 2014). The application of hydraulic fracturing requires high volumes of water and therefore has the potential to promote a high demand for freshwater, induce groundwater contamination, and require significant expenses in wastewater disposal (Miller et al., 2013).

Hydraulic fracturing is used to created fractures, or cracks, in the formation to facilitate the release of natural gas and oil, while long horizontal laterals drilled by using horizontal drilling increases the contact area between the formations and the hydraulic fracturing fluids (Li et al., 2015). The amount of water used in hydraulic fracturing is not simply related to the vertical depth of well, but it is also dependent on the shale plays, operators, the lateral lengths, and the number of "fracking" stages (Nicot and Scanlon, 2012). A number of factors, including formation geology, product amount, and number of fracture stages, may affect the quantity of water required to fracture a well (Kuwayama et al. (2015). Previous studies have found that the mean water used per well for oil production in the Eagle Ford was twice what was needed to stimulate wells located in the Bakken shale play because of the geological differences and the higher

productions, instead of the water-to-oil ratios (Scanlon et al. (2014a), while it has been suggested that there is a strong correlation between water use and gas production in shale gas wells (Nicot and Scanlon (2012). In July 2011, the U.S. Energy Information Administration. (2011) reported there was a total of 21.24 trillion m^3 and 3.82 billion m^3 of technically recoverable shale gas and oil in U.S. 86% of the technically recoverable shale gas reservoirs are located in the Northeast, Gulf Coast, and Southwest regions (U.S. Energy Information Administration., 2011).

When hydraulic fracturing fluids are injected into the formation the public is usually concerned with the potential for these fluids to contaminate groundwater, especially aquifers used as sources of drinking water (Briskin, 2015). Hydraulic fracturing fluids under pressures higher than 68,948 kPa can easily extend the induced fractures into the surrounding areas (Jackson et al., 2015). An adequate vertical separation between hydraulic fracturing operations and aquifers must be maintained for shallow hydraulic fracturing wells, which pose a higher risk of contamination compared to deeper wells (Jackson et al., 2015). The fluids returning back to the surface after releasing well pressure are considered to be oil and gas wastewater, and can consist of flowback (the returning hydraulic fracturing fluids) and produced water (water in the formation) (Gregory et al., 2011; Stringfellow et al., 2014). Another practice used for wastewater management involves chemical treatment prior to reuse. This consists of chemical additives, fresh water, and proppants mixed with the recycle wastewater to make up a fresh hydraulic fracturing fluid for stimulation of new wells (Wang et al., 2014).

According to Vengosh et al. (2014), the estimated volumes of wastewater per shale gas well were 3,500 m^3 in Marcellus Shale, Pennsylvania (PA) (2012), and 4,000 m^3 in Niobrara, Colorado (CO) (2012); however, Stringfellow et al. (2014) estimated the volume of flowback per well to be between 1,900-9,000 m^3. With the large volumes of water being used and returning to the surface as wastewater, recycling or reusing the water from hydraulic fracturing is considered to be a management strategy for oil and gas operations (Warner et al., 2013; Mauter and Palmer, 2014). Recycling oil and gas wastewater can reduce, not only water consumption in hydraulic fracturing (Gregory et al., 2011), but also the amount of water transported to wastewater treatment plants (WWTPs) or injected into Class II deep wells. Compared with

other applications (e.g. irrigation), wastewater can reach the requirements set for recycling into hydraulic fracturing after relatively simple treatments (Lester et al., 2015b). Increasing the amount of brackish groundwater and produced water used can alleviate the limitations on the future development of shale gas and oil production (Scanlon et al. (2014b), while decreasing the amount of freshwater usage. The large amounts of water needed for hydraulic fracturing may also contribute to the contamination of drinking water or groundwater due to inappropriate management operations (Llewellyn et al., 2015). These concerns would be more critical for the shale plays located in water scarcity regions (Kargbo et al., 2010; Nicot and Scanlon, 2012). The objective of this study was used to investigate the volume of water used in hydraulic fracturing and the vertical depth of hydraulic fracturing wells in recent years, as well as, to evaluate the use of recycled produced water by the oil and gas industry. Since most studies on hydraulic fracturing water use were focused on the Marcellus and Barnett shale plays, the objective of this study was to examine the water usage for the 14 states where the most of the hydraulic fracturing operations took place.

2.2.2. Motivations and hypothesis

Motivations:

First motivation: investigate the volume of water used in hydraulic fracturing and the vertical depth of hydraulic fracturing wells in recent years

Second motivation: evaluate the use of recycled produced water by the oil and gas industry

Hypotheses:

First hypothesis (H_0): Water volume used in hydraulic fracturing is comparable with that used in other industries in the United States.

Second hypothesis (H_0): Recycling wastewater in hydraulic fracturing which is a beneficial wastewater management has been broadly adopted.

2.2.3. Summary

Conclusions about the Hypothesis Testing:

The results obtained in this study and also related with the hypotheses are illustrated in Table 2-1, and the conclusions about the hypothesis testing are shown as follows:

1) Study in this Chapter do not support H_0 in the first hypothesis.

2) Study in this Chapter do not support H_0 in the second hypothesis.

Contributions to the Overall Hypothesis and Objective:

The second motivation and the second hypothesis were contributed to the overall hypothesis and objective. The original data downloaded from the Fracfocus is about the information of hydraulic fracturing fluids, such as water volume, chemical species and their corresponding concentrations. The volume of chemical additives and chemicals' concentration in the chemical additives were calculated based on the assumption that freshwater was mixed with the chemical additives to make up the hydraulic fracturing fluids. Wastewater in oil and gas industry for recycling is the hydraulic fracturing fluids coming back to the surface after the pressures were released, and they already contained some added chemicals. Therefore, using wastewater to replace the freshwater would reduce the usage of chemical additives.

Table 2-1 Results related with the hypotheses

Hypotheses	Results related with the hypothesis
First hypothesis	• The state with the largest percentage of water used in hydraulic fracturing was North Dakota (1.78%) in 2014. • The proportions of thermoelectric power in total state water use were 76.48% in Ohio, 73.01% in Arkansas, 72.78% in North Dakota, 69.97% in West Virginia, 66.30% in Pennsylvania, 51.89% in Louisiana, and 45.00% in Texas. • The proportions of irrigation in total state water use were 93.59% in Montana, 92.98% in Wyoming, 88.28% in Colorado, 85.44% in New Mexico, 76.00% in Kansas, and 60.79% in California.
Second hypothesis	• There were 6,233 wells that reported use of recycled wastewater or produced water in the hydraulic fracturing fluids. • The annual number of wells fractured using recycled wastewater was less than 1,000, with the greatest number of wells (744) located in Arkansas in 2011. • The number of wells fractured with recycled wastewater was zero in Kansans (except 2012), in Montana (except 2014), in North Dakota (2009-2012), and in New Mexico (2009-2012). • The median values (ignoring zero) for the recycled wastewater volume percent and the number of wells are 6.55% and 10.84%, respectively.

Strengths:

1) In the studied database, there were 80,047 fractured between 2008 and 2014 and distributed in 14 states. The data in this study is mega and reprehensive.

2) The data about water/wastewater usage reported in the literature were included and compared with the data obtained in our study.

Limitations:

1) The water availability was not investigated in our study. When the wells located in the water scarcity areas, the available water would be limited. It will enhance the water competitions among different industries, although the percentage of water used in hydraulic fracturing with the total state water use were generally small in our study.

Future Directions:

Based on the conclusions from our study, recycling wastewater had not been widely adopted by 2014. It is considered as one of the most beneficial wastewater managements, and future studies on reducing the cost for recycling wastewater and increasing the percentages of recycling wastewater in the hydraulic fracturing fluids would benefit the environment greatly.

2.3. Database and Tools

The data for this study was obtained from www.FracFocus.org (FracFocus, 2015). The website is managed by the Groundwater Protection Council and Interstate Oil and Gas Compact Commission. Natural gas and oil companies use the website to disclose data for each well that is put into production through hydraulic fracturing. The database includes wells that recover oil and natural gas. A total of 80,968 portable document format (PDF) files from 14 states were downloaded from FracFocus between January 5, 2015 and March 18, 2015.

MATLAB version R2014b (The MathWorks, Natick, MA) was used to import the data from 80,968 PDF files into an Excel spreadsheet (Microsoft Office 2013, Microsoft Corporation, Redmond, WA). The database consisted of 20 variables including: Fracturing Date, State, County, API Number, Operator Name, Well Name and Number, Longitude, Latitude, Long/Lat Project, Production Type, True Vertical Depth (ft.), Total Water Volume (gal), Trade Name, Suppler, Purpose, Ingredients, CAS Number, Max Additive Concentration (%), Max Concentration In Hydraulic Fracturing Fluids (%), and Comments. The wells were identified by: Fracturing Date, State, County, American Petroleum Institute (API) Number, Operator Name, Well Name and Number, Longitude, Latitude, and Long/Lat Project (used for the GIS software).

A summary of the database is available in Table A-1 found in the Appendix A. Although 80,968 Excel files were imported, the database used to organize the information had a total of 80,164 wells. This was due to the fact that some wells were determined to be duplicates based on the previously mentioned identifiers. Of the 80,164 wells, 80,047 were fractured between 2008 and 2014, which are listed in Table A-2 (in the Appendix A) while the others were fractured either before 2008 or in the beginning of 2015. Only 79,840 of 80,047 wells reported the total water volume (illustrated in Figure 2-1), while 73,633 of 80,047 wells presented the vertical depth. For the True Vertical Depth, four wells (two wells in Texas (TX), one well in Pennsylvania, and one well in West Virginia (WV)) with the vertical depths larger than 3.05 Mm and three wells in Texas with vertical depths smaller than 3.05 m. were considered as outliners and were not included when analyzing the vertical depth. For the Total Water Volume, two wells in Texas and one well in Oklahoma (OK) with water volumes greater than 3.79 Mm^3 or less than 0.038 m^3 were considered as outliners and were not used in the calculations to determine the amount of water used.

The wells fractured between 2008 and 2014 were analyzed in this study by MATLAB with a Statistics Toolbox. Origin 9.1 (OriginLab Corporation, Northampton, MA) was used to develop the graphs, while ArcGIS 10.2 (ESRI, Redlands, CA) was used to plot the location of wells on the Geographic Information System (GIS) map according to their Longitude, Latitude, and Long/Lat Project. Three data coordination systems were used in the database and include the North American Datum of 1927 (NAD27), the North American Datum of 1983 (NAD83), and World Geodetic System of 1984 (WGS84). Before the GIS plotting, the data was converted into NAD83. The different data were used because of the assumptions and measurements utilized by the coordination systems, which can make locations with identical latitude and longitude appear to be in different positions on the earth.

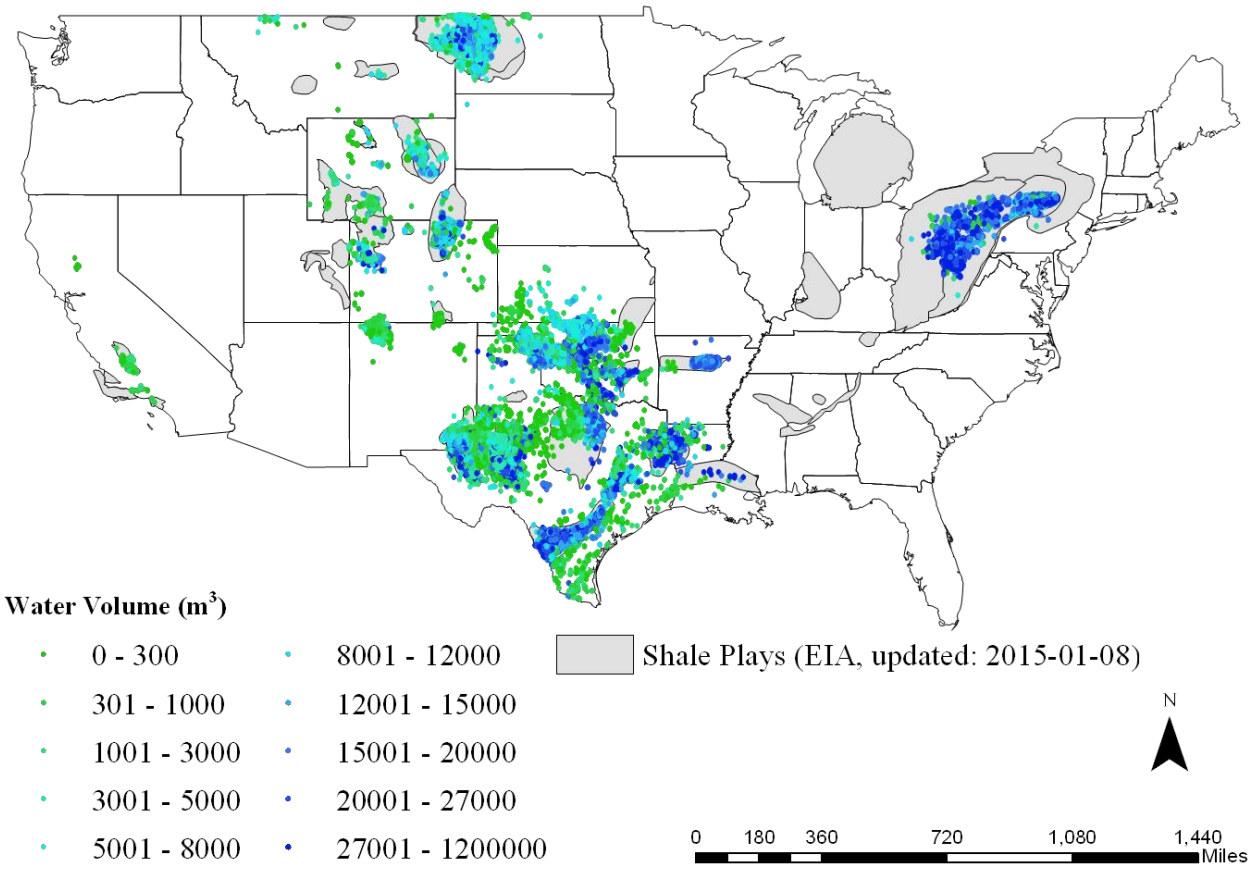

Figure 2-1. Shale plays in the United States. Source: U.S. Energy information administration, http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/maps/maps.htm, accessed on 03/18/2015. Water usage for wells put into production from 2008 to 2014 using hydraulic fracturing and reported by the natural gas industry are grouped by the water volume (m^3) and are shown in the blue and green. The coordination system used in this map is North American Datum (NAD83) provided by U.S. EIA.

2.4. Results and Discussion

2.4.1. Volume of Water Use and Vertical Depth in Hydraulic Fracturing

2.4.1.1. Cumulative Water Use

Marcellus, Haynesville, and Barnett are the largest shale gas plays in the studied regions as shown in Figure 2-1. The state distribution of shale plays is showed in Table A-2 (in the Appendix A). Marcellus is mainly under the states of West Virginia, Pennsylvania, Ohio (OH), and New York (NY) (Lee et al., 2011), while Barnett is located in Bend Arch-Ford Worth Basin, Texas (Pollastro et al., 2007). The cumulative amounts of water used and cumulative number of wells in each state are shown in Table 2-2, Figure A-1 and Figure A-2 located in the Appendix A. From 2008 to 2014, 929.98 Mm^3 water was used to fracture 80,047 wells located in 14 states studied. In Texas alone 457.42 Mm^3 of water was used to fracture 40,521 wells between 2008 and 2014. In Pennsylvania about 108.67 Mm^3 of water was used in the treatment of 5,127 wells. From 2008 to 2014, there were 7,978, 6,765, and 5,919 wells were fractured in Colorado, Oklahoma, and North Dakota (ND), respectively. The water volume used to fracture these wells was between 63.03 and 82.23 Mm^3. On average the amount of water used in Colorado, Oklahoma and North Dakota was less than what was used to facture a well in Pennsylvania. At the same time, there were more wells put into production in each of the three states than in Pennsylvania. California (CA) used 0.93 Mm^3 of water to fracture 1,923 wells, which is less than the 28.50 Mm^3 of water to put 1,381 wells in production in Louisiana (LA), and the 30.23 Mm^3 of water for the 1,026 wells in fractured West Virginia.

Table 2-2. Cumulative water use for wells put into production through hydraulic fracturing in 14 states from 2008 to 2014.

State	Cumulative water Use (Mm^3)	Number of Wells
Arkansas (AR)	48.41	2,507
California (CA)	0.93	1,923
Colorado (CO)	63.83	7,978
Kansas (KS)	3.02	539
Louisiana (LA)	28.50	1,381
Montana (MT)	3.50	467
North Dakota (ND)	63.03	5,919
New Mexico (NM)	9.26	2,300
Ohio (OH)	21.30	838
Oklahoma (OK)	82.23	6,765
Pennsylvania (PA)	108.67	5,127
Texas (TX)	457.42	40,521
West Virginia (WV)	30.23	1,026
Wyoming (WY)	9.66	2,756
Total	929.98	80,047

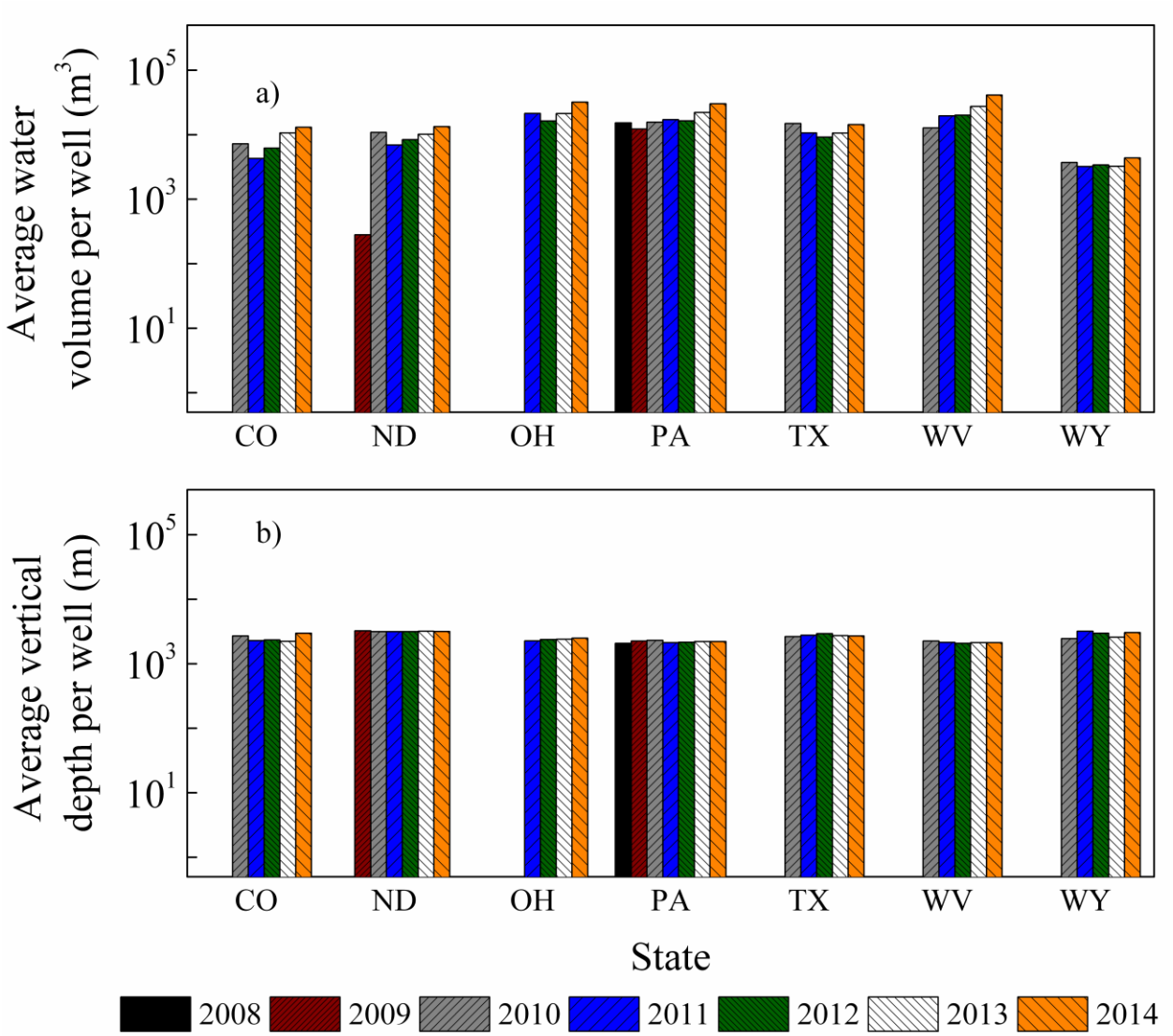

Figure 2-2. The average amount of water used per well per year to put a well into production in CO, ND, OH, PA, TX, WV, and WY: a) Average volume of water used per well and b) Average vertical depth per well in wells which reported the vertical depths.

Cumulative water use has been reported in the Barnett Shale located in Texas (Nicot and Scanlon, 2012; Nicot et al., 2014), the Eagle Ford Shale Play located in Texas (Scanlon et al., 2014a), and the Bakken Shale Play located in North Dakota, Montana (MT) (Scanlon et al., 2014a) (Table A-3 in the Appendix A). The estimated water use for Barnett was 145 Mm^3 for around 15,000 wells between 2000 to mid-2011 (Nicot and Scanlon, 2012), and 210 Mm^3 between 1981 and 2012 (Nicot et al., 2014). Scanlon et al. (2014a) reported the cumulative amounts of water use were ~150 Mm^3 for 8,301 wells in the Eagle Ford Shale Play (2009-2013), and ~59.81 Mm^3 for 7,868 wells in the Bakken (2005-2013). This study determined that there were 56.06 Mm^3 of water used for 5,261 wells by the end of 2011, 152.91 Mm^3 water used for 15,811 wells by the end of 2012, and 291.31 Mm^3 water used for 28,929 wells by the end of 2013 in Texas. By the end of 2013, North Dakota and Montana used 34.59 Mm^3 and 2.32 Mm^3 water on 3,779 and 352 wells, respectively. Both the number of wells and the water volumes reported in this study are smaller than those values previously reported value.

2.4.1.3. Annual Water Use

The volume of water used in each state annually from 2008 to 2014 is shown in Figure A-3 and Figure A-4 (in the Appendix A). The number of wells put into production in all states during that time increased from 2 to 24,527 by 2013. However, in 2014 the number of wells decreased to 22,675 and is reflected in Figure A-3.a, Figure A-4.a, and Table A-2. There were more than 1,000 and less than 10,000 wells fractured annually in Colorado (2011-2014), North Dakota (2012-2014), Oklahoma (2012-2014), Pennsylvania (2011-2014), and Texas in 2011. In Figure A-3.b and Figure A-4.b, the annual water use was larger than 10 Mm^3 in Arkansas (AR) (2011, 2012), Colorado (2011-2014), Louisiana in 2011, North Dakota (2012-2014), Ohio in 2014, Oklahoma (2012-2014), Pennsylvania (2011-2014), Texas (2011-2014), and West Virginia in 2014. Texas used 96.85 Mm^3 water in 2012, 138.41 Mm^3 water in 2013, and 166.10 Mm^3 water in 2014, because their annual numbers of fractured wells were larger than 10,000. The median (ignoring zero values) of the annual water use is 2.76 Mm^3. The annual water use displays the increasing trends in all the studied states, except Arkansas, California, Louisiana, and Wyoming (WY). Murray (2013) estimated the water used for hydraulic fracturing in Oklahoma was 16.3 Mm^3 in 2011 with a median of 11,350 m^3 per

well. This study shows Oklahoma used 7.83 Mm^3 of water for 542 wells in 2011, with an average 14,438 m^3 water per well.

2.4.1.4. Annual Average Water Use per Well

Water use in hydraulic fracturing has been a major concern (Scanlon et al., 2014a) as the amount is estimated at ~7,571-~18,927 m^3 per well drilled. In this study (Figure 2-2.a, Figure A-5.a, and Table A-5 in the Appendix A), most of states showed more than 1,000 m^3 and less than 30,000 m^3 of water used per well. The median (ignoring zero values) of annual average water use per well is 11,259 m^3. Jackson et al. (2015) reported the mean and median water volumes of 9,199 m^3 and 5,754 m^3, respectively, per well were used to fracture approximately ~44,000 wells from 2010-2013. The annual average water use per well increased year by year in Montana from 5,085 m^3 in 2011 to 11,259 m^3 in 2014, in New Mexico (NM) from 1,759 m^3 in 2011 to 7,157 m^3 in 2014, in West Virginia from 12,695 m^3 in 2010 to 41,337 m^3 in 2014. The increasing annual water use per well may be induced by the increasing trends in lateral lengths, the number of fracking stages, or production (Murray, 2013; Scanlon et al., 2014a). These driving factors will need to be verified with more data consisting of well characteristics (Bibby et al., 2013).

The annual water use per well was 3,215-4,373 m^3 in Wyoming (2010-2014) and 423-1,030 m^3 in California (2011-2014), which were relatively lower compared with other states in this study. The water use per well has also been reported in other studies and is shown in Table A-6. In 2012, 13,000 m^3 water per well was used to fracture the wells in the Niobrara Shale play in Colorado, which is almost twice the volume of water used per well found in this study (Vengosh et al. (2014). The amount of freshwater consumed over the life cycle of a Marcellus Shale gas well was between 6,700-33,000 m^3 with an average water volume of 20,000 m^3 (Jiang et al. (2014). This was less than the 7,700-38,000 m^3 of water reportedly used to fracture wells located in the Marcellus Shale play (Kargbo et al. (2010). The average amount of water used annually per well in this study ranged from 12,213-30,252 m^3 in Pennsylvania, 12,695-41,337 m^3 in West Virginia, and 16,261-31,988 m^3 in Ohio, which are similar to the previously reported values (Kargbo et al., 2010; Jiang et al., 2014).

2.4.1.5. Water Usage and Vertical Depth

Figure 2-2.b and Figure A-5.b show the changes of the average vertical depths of the wells during each year for each state. As shown in the figures, the changes in the well depths showed little variations for each year. The annual average vertical depths (excluding the zero annual average vertical depths) were 975-1,280 m in Arkansas, 712-871 m in California expect 1,489 m in 2011, 2,230-2,974 m in Colorado, 1,377-1,540 m in Kansas (KS), 3,492-3,957 m in Louisiana, 2,802-3,277 m in Minnesota, 3,137-3,252 m in North Dakota, 1,992-2,283 m in New Mexico except 4,225 m in 2009, 2,263-2,501 m in Ohio, 2,047-3,274 m in Oklahoma, 2,072-2,304 m in Pennsylvania, 2,639-2,920 m in Texas, 2,079-2,256 m in West Virginia, and 2,450-3,196 m in Wyoming. For this study, it was determined that the greatest average vertical depth was located in the Haynesville field in Louisiana (which is one of the deepest shale plays) however the relative subsurface depths of the Haynesville shale play is between 3,353-4,420 m and are located in both northeast Texas and northwest Louisiana (Thompson et al., 2011).

Correlations between the vertical depth and water usage are illustrated in Figure A-6. The figure shows that the water usages are not related with the vertical depth. Hydraulic fracturing wells coupled with horizontal drilling technology are drilled vertically to set depths of the shale stratum, which is the vertical depth of the well (Weltman-Fahs and Taylor, 2013; Li et al., 2015). The vertical depth of the wells did not vary greatly in each state, but due to the location of the in the shale formations, the lengths of the horizontal laterals range from 457m to 3048 m (Dale et al., 2013). Variability in the water usage could be due to the length of the horizontal laterals (Gallegos et al., 2015); therefore, it may be beneficial for the industry to report the length of the horizontal laterals for each well.

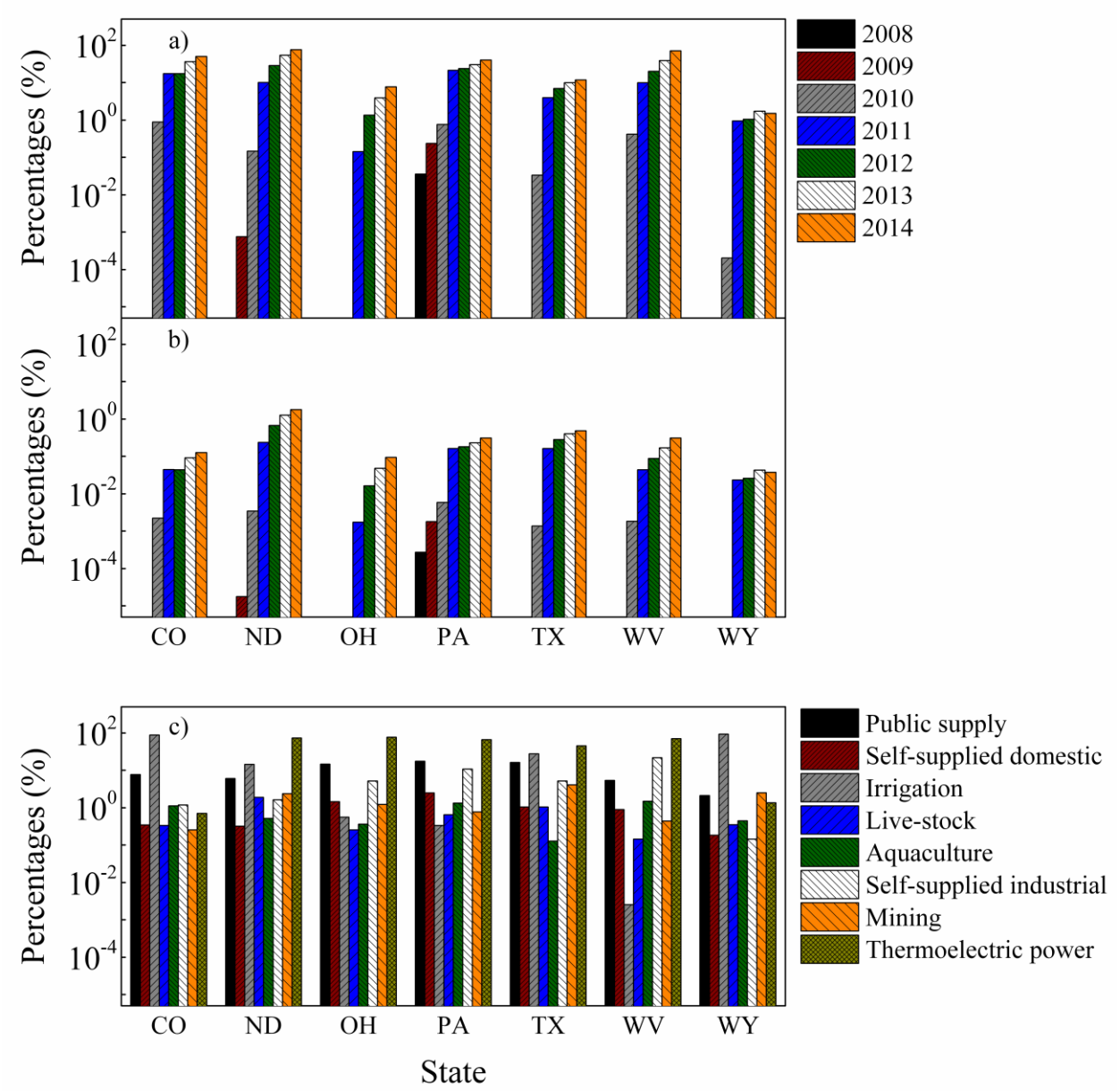

Figure 2-3. Percentage of freshwater use in CO, ND, OH, PA, TX, WV, and WY: a) Hydraulic fracturing versus mining; b) Hydraulic fracturing versus total state water use; c) Water users versus total state water use.

2.4.2. Components of Water Use in Hydraulic Fracturing

2.4.2.1. Freshwater

Freshwater is the major component of the total water used in hydraulic fracturing (Jiang et al., 2014; Nicot et al., 2014). The percentage of water used for hydraulic fracturing in each state was calculated by applying the total amounts of water in each state reported by the U.S. Geological Survey (USGS) in 2010 (Maupin et al., 2014) are shown in Table A-7. According to Maupin et al., the mining water reported is the water employed for extracting minerals, such as coal, iron, sand, gravel, petroleum, and natural gas (Maupin et al., 2014). Based on the increments of hydraulic fracturing water use from 2008 to 2014, the proportions of freshwater used in hydraulic fracturing with that in mining showed increasing trends in most of the states as illustrated in Figure 2-3.a and Figure A-7.a (in the Appendix A). In 2014, those proportions were calculated to be 49.53% in Colorado, 76.00% in North Dakota, 40.26% in Pennsylvania, 11.75% in Texas, and 70.45% in West Virginia. According to the percentages calculated, most of the water used for mining in those states was actually used for hydraulic fracturing. This proportion reduced from 44.12% in 2011 to 18.03% in 2014 in Arkansas, and dropped from 74.34% in 2011 to 25.59% in 2013 and then rose to 28.59% in 2014 in Louisiana. This reduction may be due to a number of factors including the replacement of the freshwater with recycled wastewater and the decrease in natural gas production in the shale plays of Fayetteville and Haynesville, which is presented in Figure A-8 in the Appendix A (U.S. Energy Information Administration, 2015).

Figure 2-3.b and Figure A-7.b (in the Appendix A) show the annual percentages of freshwater used in hydraulic fracturing for each state in this study. The state with the largest percentage of water used in hydraulic fracturing was North Dakota (1.78%) in 2014. The percentages of freshwater used Oklahoma, Texas, West Virginia, Pennsylvania, and Colorado in 2014 were 0.67%, 0.48%, 0.31%, 0.31%, and 0.13%, respectively. The percentages of freshwater used for fracturing in California (0.000176%-0.000500%) were much lower than the rest of the states. These percentages are consistent with the low values reported by (Nicot and Scanlon, 2012; Nicot et al., 2014). Water use in the Barnett Shale play in 2010 accounted for ~9% of water used in Dallas (Nicot and Scanlon, 2012), and the amount of water used in the Barnett shale

(2011) was 32 Mm^3 making up about 0.2% of the state's water consumption in 2011 (Nicot et al., 2014). The proportions of thermoelectric power in total state water use were 76.48% in Ohio, 73.01% in Arkansas, 72.78% in North Dakota, 69.97% in West Virginia, 66.30% in Pennsylvania, 51.89% in Louisiana, and 45.00% in Texas, which is shown in Figure 2-3.c and Figure A-7.c (in the Appendix A), and the proportions of irrigation in total state water use were 93.59% in Montana, 92.98% in Wyoming, 88.28% in Colorado, 85.44% in New Mexico, 76.00% in Kansas, and 60.79% in California. This suggests though the process of hydraulic fracturing uses millions of cubic meters of freshwater at one time, the amount of water used annually is relatively lower than the water used by other industries.

2.4.2.2. Recycled Wastewater

Increasing recycled wastewater volume and decreasing freshwater demand would alleviate the effect of water scarcity on shale energy development. Figure 2-4 shows the locations of the wells where recycled flowback fluid, produced water or wastewater was used in the fluids for well stimulation. There were 6,233 wells that reported use of recycled wastewater or produced water in the hydraulic fracturing fluids. Of these wells 6,221 were fractured between 2008 and 2014. The volume of recycled wastewater used to fracture the wells found in Figure 2-4 was categorized in the same manner as seen in Figure 2-1. Figure 2-5, Figure A-9, and Figure A-10 (in the Appendix A) show the number of wells and amount of recycled wastewater for the wells from 2009 to 2014 in each state. Use of recycled wastewater was not reported in the states studied until 2009. The annual number of wells fractured using recycled wastewater was less than 1,000, with the greatest number of wells (744) located in Arkansas in 2011. The number of wells fractured with recycled wastewater was zero in Kansans (except 2012), in Montana (except 2014), in North Dakota (2009-2012), and in New Mexico (2009-2012). The greatest amount of recycled wastewater was 5.52 Mm^3 in Colorado (2012), while the maximum of recycled wastewater volume per well was 65,925 m^3 in Louisiana (2014). The median volume of recycled wastewater per well (ignoring zero) was 7,127 m^3, which was more than half of 11,259 m^3, the median value of water used per well. This indicates that over half of the water used to fracture these wells came from recycled wastewater.

Figure 2-6 (and Figure A-11 in the Appendix A) shows the average percentage of recycled wastewater in each state from 2009 to 2014. The annual average percentage of recycled wastewater used instead of freshwater (excluding the zero annual average percentages) ranged from 22.28-53.23% in Arkansas, 2.31%-32.16% in California, 12.04%-45.43% in Colorado, 6.40%-27.04% in Pennsylvania, and 1.81-99.74% in Wyoming. The median values (ignoring zero) for the recycled wastewater volume percent and the number of wells are 6.55% and 10.84%, respectively. The percentage of wells fractured with recycled wastewater in Ohio and Arkansas was higher than the other states in this study. Almost all of the wells in Arkansas and half of wells in Ohio were fractured with recycled wastewater. The percentage of wells put into production by using recycled wastewater increased from 20.00% in 2009 to 40.35% in 2010 but decreased to 13.55% in 2014 in Pennsylvania. The decreasing trends were also seen in Louisiana, Ohio, West Virginia, and Wyoming. Rozell and Reaven (2012) showed only 16% of the 729,000 m^3 of hydraulic fracturing wastewater reported in Marcellus Shale from July 2009 to June 2010 was recycled. The volume of recycled wastewater used in wells fractured in Pennsylvania in this study was 43,542 m^3 in 2009 and 241,596 m^3 in 2010, accounting for 17.83% and 27.04% of water use in 2009 and 2010, respectively. Before 2011, 13% of the wastewater from conventional and Marcellus wells in Pennsylvania was recycled and then increased to 56% in 2011 (Lutz et al. (2013). Recycled wastewater made up 9.87% of the water used and 32.29% of the wells put into production by hydraulic fracturing in Pennsylvania in 2011 used fluids consisting of the recycled wastewater.

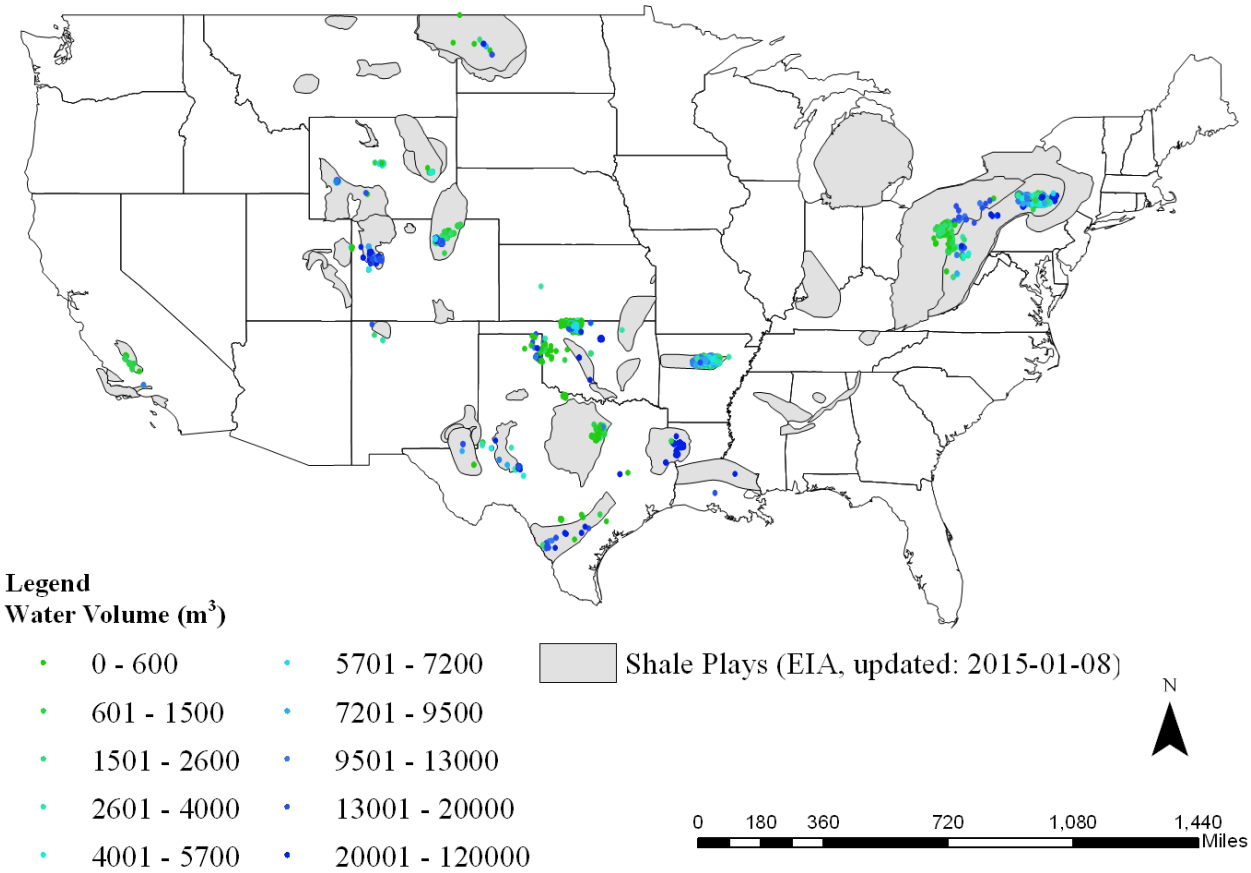

Figure 2-4. Location and amounts of recycled wastewater used for hydraulic fracturing. Wells are grouped according to the volume of water used (Unit: m^3). The coordination system used in this map is North American Datum (NAD83) provided by U.S. EIA.

Figure 2-5. Amount of recycled wastewater used for hydraulic fracturing fluids. a) Volume of recycled wastewater; b) Average amount of recycled wastewater per well.

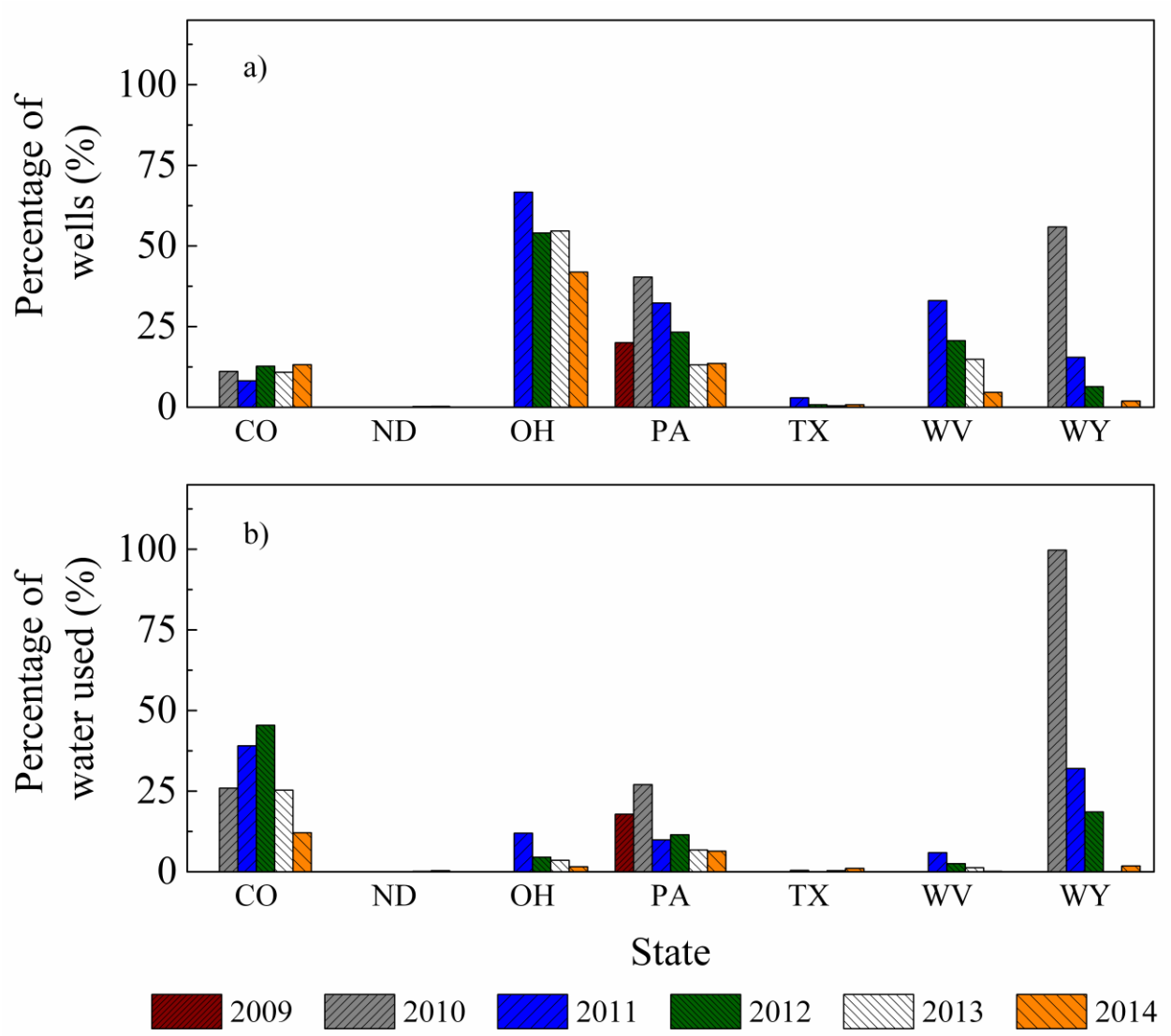

Figure 2-6. Recycled water used for hydraulic fracturing stimulation of wells in each state. a) Percentage of put into production using recycled water with respect to the total wells completed in each state; b) Percentage of water volume being recycled with respect to the total water used during well completion.

The treatments for hydraulic fracturing wastewater vary by shale plays however; there are several methods for handling the wastewater from hydraulic fracturing including transporting to offsite treatment facilities, injecting the water into Class II wells (deep subsurface wells), and *on-site* recycling or reusing (Harkness et al., 2015). The dominant treatment/disposal methods in Marcellus Shale in the past involve transporting the water to a treatment facility to remove solids then reusing the treated water for further fracturing practices or recycling/reusing (Nicot et al., 2014). Roughly 83% of the hydraulic fracturing wastewater from the Marcellus shale play was sent to treatment facilities while 16% of the wastewater was recycled/reused between July 2009 to June 2010 (Rozell and Reaven, 2012).

Although recycling wastewater is considered the best beneficial method (Gregory et al., 2011; He et al., 2014), the percentages of recycled wastewater in this study were generally low as seen in Figure 2-6 and Figure A-11. Scanlon et al. (2014b) suggested reusing or recycling wastewater was limited in the Eagle Ford play because the volumes recovered were less than 5% of the water demand during the first month of production. Dale et al. (2013) also reported the wastewater was ~20% of freshwater requirements in the Marcellus Shale, due to the flow-back rates and increased drilling. Decreased amounts of water recovered, as well as the high total dissolve solids (TDS) concentrations, potential radioactive elements, and organic substances (Balaba and Smart, 2012; Haluszczak et al., 2013), have limited the potential for recycling hydraulic fracturing wastewater (Wang et al., 2014). Precipitates, such as $CaCO_3$, $BaSO_4$, $Fe(OH)_3$, may be formed by injecting flowback or produced water in the wellbore, and the high TDS concentrations may reduce the effectiveness of friction reducers, fracture permeability and overall gas production (Gregory et al., 2011; Lester et al., 2015b).

2.5. Conclusions and Future works

The water usage among hydraulically fractured wells from 2008 to 2014 in 14 states was investigated in this study. Approximately 930 Mm^3 of water were used to hydraulically fracture 80,047 wells during that time. Of the 930 Mm^3, the 40,521 wells put into production in Texas required approximately half the amount of water, followed by Pennsylvania with 1.09×10^8 m^3 for 5,127 wells. The annual water use increased along

during the 6-year period for most of the states. The annual average water use per well in most of states was 1,000-30,000 m^3.

The percentage of freshwater used in hydraulic fracturing for each state was relatively lower than the amount of water used by other industries, including agricultural irrigation and thermoelectric power. However, over half of the fractured wells were shown to be located in the regions with high or extremely high water stress (Freyman and Salmon, 2013; Freyman, 2014). Currently, the water availability measured by criticality ratio neglects the groundwater as the water resource, which may overstate the conditions of the water supply (Alcamo et al., 2000; Jarvis, 2013). In order to alleviate the need for freshwater, many companies are reusing the wastewater for future unconventional gas production, however; of the 80,047 wells in this study, only 6,221 reported recycled wastewater volumes as part of their hydraulic fracturing fluids, which is less than 10% of the wells put into production at the time of this study. In a number of states, there was no recycling of the wastewater reported suggesting that this measure has yet to be adopted due to the low volumes of produced/flowback water returning and the high cost in treatments for recycling.

CHAPTER 3

CHARACTERIZATION OF THE CHEMICALS USED HYDRAULIC FRACTURING FLUIDS FOR WELLS LOCATED IN THE MARCELLUS SHALE PLAY

A version of this chapter is prepared for a publication:

Chen, H. and K. E. Carter (2016). "Characterization of the Chemicals Used Hydraulic Fracturing Fluids for Wells Located in the Marcellus Shale Play" (submitted to *Journal of Environmental Management*)

Highlights

- 517 chemicals were used for fracturing in the Marcellus Shale Play.
- Many toxic organics were found in hydraulic fracturing fluids.
- Most of the added chemicals can be removed when adopting appropriate treatments.

3.1. Abstract

Hydraulic fracturing, coupled with the advances in horizontal drilling, has been used for recovering oil and natural gas from shale formations and has aided in increasing the production of these energy resources. The large volumes of hydraulic fracturing fluids used in this technology contain chemical additives, which may be toxic organics or produce toxic degradation byproducts. This paper investigated the chemicals introduced into the hydraulic fracturing fluids for completed wells located in Pennsylvania and West Virginia from data provided by the well operators. The results showed a total of 5,071 wells, with average water volumes of 5,383,743 ± 2,789,077 gal (mean ± standard deviation). A total of 517 chemicals were introduced into the formulated hydraulic fracturing fluids. Of the 517 chemicals listed by the operators, 96 were inorganic compounds, 358 chemicals were organic species, and the remaining 63 cannot be identified. Many toxic organics were used in the hydraulic fracturing fluids. Some of them are carcinogenic, including formaldehyde, naphthalene, and acrylamide. The degradation of alkylphenol ethoxylates (APEOs) would produce more toxic, persistent, and estrogenic intermediates. Acrylamide monomer as a primary degradation intermediate of polyacrylamides is carcinogenic. Most of chemicals appearing in the hydraulic fracturing fluids can be removed when adopting the appropriate treatments.

3.2. Introduction

3.2.1. Background

Shale gas has become a very important energy resource in the United States (U.S.), due to the progresses made in hydraulic fracturing and horizontal drilling technologies (Struchtemeyer et al., 2012; Zhou et al., 2014b). Hydraulic fracturing is a stimulation technique used to increase the production of oil and natural gas through the high pressure injection of fluids at high volumes to form fractures and small openings in shale formations (Struchtemeyer and Elshahed, 2012b; Struchtemeyer et al., 2012; Obo, 2013). These fluids known as hydraulic fracturing fluids are usually composed of 98% to 99.5% water and proppants (i.e. sand, resins, ceramics), with chemical additives making up the balance (Arthur et al., 2009; Gregory et al., 2011). The proppants are injected into the formations to hold the newly generated fractures open and maintaining the permeability (Gregory et al., 2011; Stringfellow et al., 2014). Chemical additives are used to reduce the friction, and bacteria growth, as well as inhibit scale buildup and corrosion of the well casing (Arthur et al., 2009; Gregory et al., 2011; Aminto and Olson, 2012).

Advancements in horizontal drilling has enabled hydraulic fracturing to become common practice for recovering oil and natural gas from shale formations (Arthur et al., 2009; Beckwith, 2010; Montgomery and Smith, 2010). However, the adverse environmental impacts of this technology on the groundwater and surface water have gradually attracted the concerns of many engineers and scientists (Arthur et al., 2009; Gregory et al., 2011). One of the concerns is the return of the injected hydraulic fracturing fluids to the surface once the pressure is released. This fluid is generically referred to as flowback or produced water; however, flowback commonly refers to hydraulic fracturing fluids that return to the surface immediately after fracturing and before production, while produced water relates to hydraulic fracturing fluids and formation fluids that return during production and can take place over long time periods (Barbot et al., 2013; Stringfellow et al., 2014). The composition of both the flowback and produced waters varies due to the differences in the amounts and types of chemical additives used in the hydraulic fracturing fluids, the location within the geological characteristics of sites the fluids are injected, and the chemical characteristics

of the supplied water (Aminto and Olson, 2012; Barbot et al., 2013). Because of the differences and the potential for the chemical additives to be toxic or contribute to the formation of toxic byproducts, a careful and systematic examination of the chemicals added in hydraulic fracturing fluids is necessary for processing and managing the hydraulic fracturing fluids avoiding ecological damages (Stringfellow et al., 2014). This paper investigated the characteristics of hydraulic fracturing fluids in wells located in West Virginia and Pennsylvania including the number of wells, total water volume and the toxicity and degradability of the organic compounds introduced through the chemical additives.

3.2.2. Motivations and hypothesis

Motivations:

First motivation: investigate the types of chemicals added in hydraulic fracturing fluids (*i.e.* chemical species, the number of wells added a specific chemical and its frequency, average concentrations) in wells located in West Virginia and Pennsylvania

Second motivation: analysis the toxicity and degradability of the introduced organic compounds

Hypotheses:

First hypothesis (H_0): Toxic and even carcinogenic organics are added into the hydraulic fracturing fluids.

Second hypothesis (H_0): Some of the introduced organic compounds are persistent in the aqueous phase.

Third hypothesis (H_0): The toxic and persistent organics cannot be removed from the wastewater in the oil and gas industry.

3.2.3. Summary

Conclusions about the Tested Hypotheses:

The results obtained from this Chapter and related with the tested hypotheses are presented in Table 3-1, and the conclusions about the tested hypotheses are shown as follows:

1) The study in this Chapter do support H_0 in the first hypothesis.
2) The study in this Chapter do support H_0 in the second hypothesis.

3) The study in this Chapter do not support H_0 in the third hypothesis.

Contributions to the Overall Hypothesis and Objective:

The second motivation and the first hypothesis are contributed to the overall hypothesis and objective. When the toxic chemicals are used for the hydraulic fracturing, they would pose the adverse health effects to human through inhalation or skin contact. If the toxic chemicals are not used, the workers in the hydraulic fracturing wells would not have the possibility to be exposure to those toxic chemicals.

Table 3-1 Results related with the hypotheses

Hypotheses	Results related with the hypothesis
First hypothesis	• Formic acid (CAS: 64-18-6), reported to be in 254 wells with a mean concentration of 21.2 ppm, is toxic to microorganisms and humans. • Formaldehyde (CAS: 50-00-0), reported in 556 wells with a mean concentration of 1.2 ppm, is a VOC. It is widely used as a disinfectant and was classified as "carcinogenic to humans" (Group 1) by the International Agency for Research on Cancer (IARC) (WHO, 2006). • Naphthalene (CAS: 91-20-3), added in 144 wells with a mean concentration of 0.59 ppm, is one of the typical polycyclic aromatic hydrocarbons (PAHs) found in hydraulic fracturing fluids. It was classified as a possible carcinogen (Group 2B) by IARC, due to the fact that there is insufficient or inadequate evidence of its potential carcinogenic effects on animals and humans (WHO, 2002). • …
Second hypothesis	• Three isomers of xylene, benzene, toluene, ethylbenzene, and xylene, together notoriously known as BTEX, are the most persistent gasoline compounds (Osterreicher-Cunha et al., 2009; Huang and Li, 2014). Xylene (CAS: 1330-20-7) was found in the hydraulic fracturing fluids for the treatment of 47 wells with a mean concentration of 1.6 ppm. • Benzalkonium chloride (CAS: 68424-85-1), found in 1,046 wells with a mean concentration of 19.5 ppm, is used as a disinfectant(Bassarab et al., 2011) and belongs to quaternary ammonium compounds (QACs). Benzalkonium chloride is persistent because it tends to be adsorbed on the sludge in WWTPs and not biodegradable under anaerobic condition (Tezel and Pavlostathis, 2009). • …
Third hypothesis	• *Aspergillus nomius* SGFA1 and *Penicilium chrysogenum* SGFA3, isolated from untreated sewage sediments in formaldehyde-contaminated areas, degraded 3,000 and 9,000 mg/l of formaldehyde completely within 7 days, respectively (Yu et al., 2014). • Suchithra et al. (2015) found benzalkonium chloride (100 mg/l) was completely mineralized within 2 hours by using hybridization of activated carbon onto TiO_2. • …

Strengths:

1) The data in this study included 5,071 wells completed between 2008 and 2014 with the last access date for wells in West Virginia and Pennsylvania was August 6 and August 22 of 2014, respectively. It is representative.

2) Most of the literatures about the toxicity and degradation of organics recovered in our database have been reviewed and summarized.

Limitations:

1) In the aqueous phase (*such as chemical additives, hydraulic fracturing fluids, and flowback wastewater*) in the hydraulic fracturing, several chemicals would exist together. The co-existing makes their toxic and degradable properties different from the corresponding properties when existing lonely in the aqueous phase.
2) The wastewater from the oil and gas industry contains high total dissolved salts (TDS) which makes its treatment more difficulty.

Future Directions:

1) Replace the toxic chemicals in the hydraulic fracturing fluids with the non-toxic chemicals without the increasing of costs.
2) Use the actual wastewater from the oil and gas industry to investigate its toxicity and degradability

3.3. Research Methods

3.3.1. Database and Tools

The Marcellus Formation (or Marcellus Shale) is currently the largest shale gas play in the United States (U.S.), with an estimated area of approximately 95,000 square miles (mi^2) and production depth ranging from 4,000 to 8,500 ft (National Energy Technology Laboratory, 2010). The formation crosses six states including West Virginia, Pennsylvania, Ohio and New York, and contains an estimated 1,500 trillion cubic feet (Tcf) of original shale gas, 489 Tcf of which was reported to be technically recoverable (National Energy Technology Laboratory, 2010; Lee et al., 2011). The data in this paper was obtained from hydraulic fracturing fluid product component information disclosures found on the www.FracFocus.org website's Chemical Disclosure Registry (FracFocus, 2014). The registry is used by well-operators as a means of disclosing the chemicals and volumes of water injected into each gas and oil well. The data gives specific locations, volumes of water and dates of completion and includes wells to produce both gas and oil. The wells used for this study were completed between 2008 and 2014 with the last access date for wells in West Virginia and Pennsylvania was August 6 and August 22 of 2014, respectively.

MATLAB version R2014b (The MathWorks, Natick, MA) was used to read the data from each well after the downloaded files were converted from portable document format (PDF) into Excel (Microsoft Office 2013, Microsoft Corporation, Redmond, WA) using Adobe Acrobat X Pro (Adobe Systems Incorporated, San Jose, CA). After importing the data into the database, it was determined that there were 111,264 observations and 20 variables including: Fracturing date, State, County, API Number, Operator Name, Well Name and Number, Longitude, Latitude, Long/Lat Project, Production Type, True Vertical Depth (ft.), Total Water Volume (gal), Trade Name, Supplier, Purpose, Ingredients, CAS Number, Max Additive Concentration (%), Max Concentration In Hydraulic Fracturing Fluids (%), and Comments. Combining MATLAB with the Statistics Toolbox, analysis and calculations were carried out and the data was then stored using Microsoft Excel 2013. Two wells in Pennsylvania, were considered as outliners due to their water volumes and vertical depths therefore, empty values were assigned to their Total Water Volume and True Vertical depth, respectively.

3.3.2. Characteristics of Disclosed Chemicals

3.3.2.1. Number of Wells versus Frequency of Chemical Observation

Observations for each compound were separated according to their CAS numbers. Observations without CAS numbers but with the same ingredient name were considered to be either the same chemical or a compound belonging to a group of similar chemicals. Many of the compounds showed up more than once in the operators' chemical disclosure lists causing the frequency in which the chemical was disclosed to be greater than the number of wells.

Observations with different values in the categories of Fracturing date, States, County, API Number, Operator Name, Well Name and Number, Longitude, or Latitude were considered to be different wells. The total number of wells was 5,071. However, when considering observations with different values in States, County, API Number, Well Name and Number, Longitude, or Latitude, there were 5,048 wells. Of those 5,048 wells, 23 wells were fractured on two different dates, which means they have the same values in States, County, API Number, Well Name and Number, Longitude, and Latitude, but different values in Fracturing date or Operator Name, therefore increasing the number of wells from 5,048 to 5,071 (See Table

A-12 in the Appendix B). Because operators use different hydraulic fracturing fluid formulations, the first method for identifying wells was adopted in the following analysis.

The value in "Num. of wells" pertains to the number of wells containing a specific chemical in their hydraulic fracturing fluid formulation. The frequency with which a chemical occurs in this paper refers to the number of incidences a specific chemical has appeared in the disclosures for the hydraulic fracturing fluids of all the wells. Since some chemicals occurred more than one time in one well, the Number of Wells is expected to be less than or equal to the Frequency in which the chemical occurs.

3.3.2.2. Mean Concentration in Hydraulic Fracturing Fluids

The mean concentration of a chemical in the hydraulic fracturing fluids (in ppm) was determined by the chemical's concentration in the hydraulic fracturing fluids of each well and the amount of water provided by the well operators for each well. In most cases the value in the variable of "Max Concentration In Hydraulic Fracturing Fluids (%)" was empty, zero, or greater than zero. Observations with empty values in the "Max Concentration In Hydraulic Fracturing Fluids (%)" or "Total Water Volume (gal)" were removed. The concentration of a chemical in hydraulic fracturing fluids of a well was calculated according to the following Equation 3-1:

Equation 3-1

$$C_{A,j} = 10^4 \times \sum_{i=1}^{m} C_{max,A,j,i}$$

Where: $C_{max,\,A,\,j,\,i}$ is the maximum concentration of chemical A in hydraulic fracturing fluids when occurring at i^{th} in well j, % by mass; m, is the frequency of chemical A in well j; $C_{A,\,j}$ is the concentration of chemical A in well j, ppm or mg/l.

"Mean Conc. in Hydraulic Fracturing Fluids, ppm" of a chemical was calculated according to Equation 3-2 and was calculated after excluding the wells with zero mean concentration.

Equation 3-2

$$C_{mean,A} = \sum_{j=1}^{n} (C_{A,j} \times V_{water,j}) \Big/ \sum_{j=1}^{n} V_{water,j}$$

Where: $C_{A,\ j}$ is the concentration of chemical A in well j, ppm; $V_{water,\ j}$ is the water volume in well j, gal; n is the total number of wells containing chemical A in their hydraulic fracturing fluids; $C_{mean,\ A}$ is the mean concentration of chemical A in wells, where chemical A was added in their hydraulic fracturing fluids, ppm or mg/l.

3.3.3. Classification

Chemicals were separated into three groups: organic compounds, inorganic compounds (Table A-13 in the Appendix B), and Unknown compounds (Table A-14 in the Appendix B). The organic chemicals were classified based on the functional groups of the chemical species and the potential for the different compounds to undergo similar chemical reactions (McMurry, 2010; Brown, 2013). ENREF 16 In order to define their characteristics, the organic compounds were classified into hydrocarbons, benzyl, phenyl, organics containing oxygen, organics containing nitrogen, sulfur, or phosphorus, and polymers. Hydrocarbons were further divided into naphthas, alkanes, alkenes, and others. Organics containing oxygen were further separated into alkoxy, ethoxy, carbohydrates & enzymes, carboxylic acids & their salts, alcohols, aldehydes, anhydrides, and others. After classifying the compounds, duplication of the chemicals was avoided by setting the priorities as follows: Ethoxy > Alkoxy > Carbohydrates & Enzymes > Polymers > Naphathas > Benzyl > Phenyl > Nitrogen > Phosphorus > Sulfur > Carboxylic Acids & their Salts. Organics with frequencies larger than or equal to 25 are discussed in this paper, while organics with frequencies less than 25 are listed in Table A-15 (in the Appendix B).

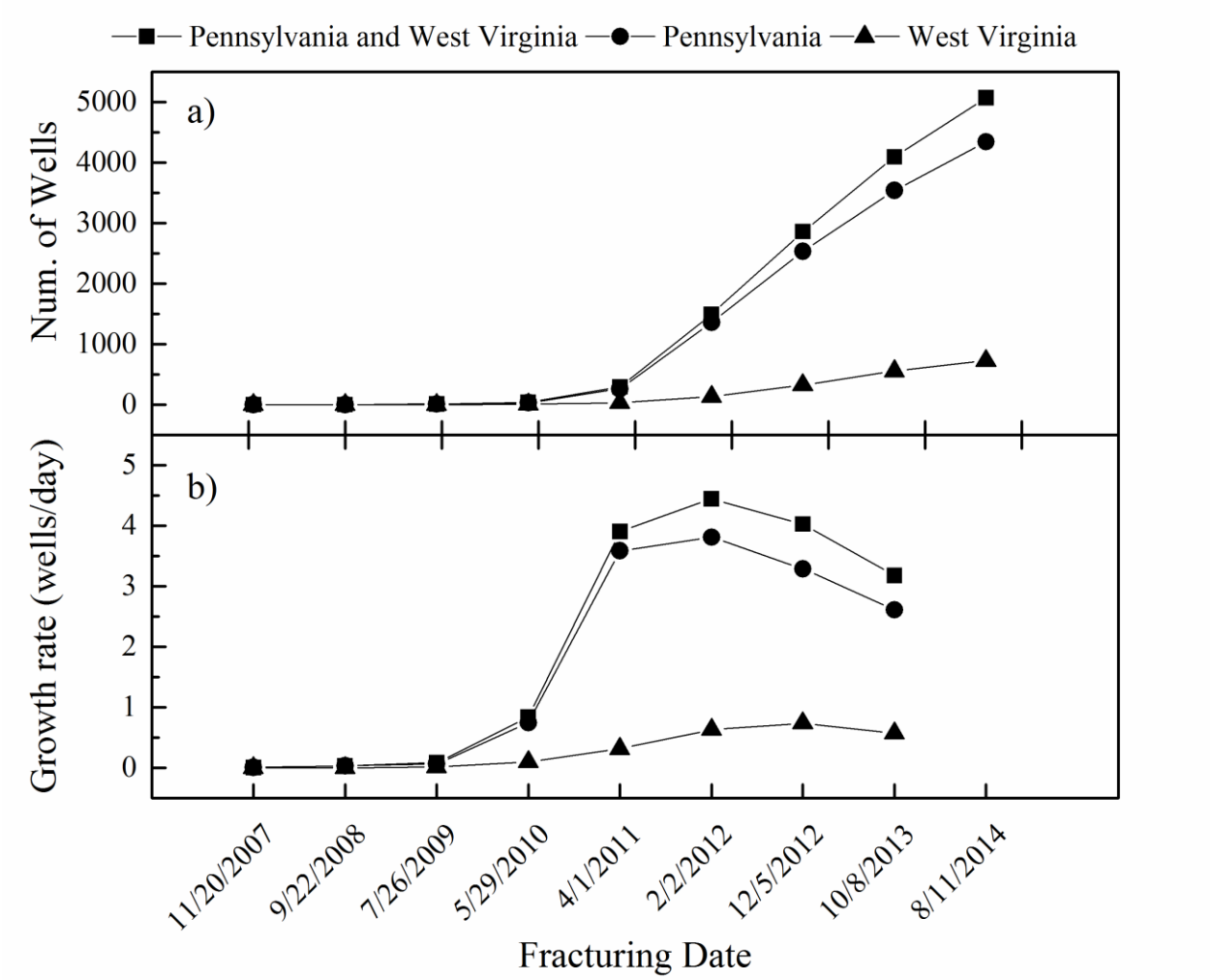

Figure 3-1. Growth in number of wells along with time.

3.4. Results and Discussion

3.4.1. Characteristics of Wells

3.4.1.1. Number of Wells Put into Production from September 2008 to August 2014

From September 2008 to August 2014, there were 5,071 reported wells located in Pennsylvania and West Virginia that were fractured; 23 of these wells were fractured twice, giving a total number of 5,048 wells. Among these wells, 4,342 and 729 are located in Pennsylvania and West Virginia, respectively. The number of wells in Pennsylvania was approximately six times greater than the number of wells completed in West Virginia. Figure 3-1.a shows the number of wells fractured in both of Pennsylvania and West Virginia, which increased from 2008 to 2014, while Figure 3-1.b shows the growth rate in the number of wells located in either Pennsylvania or West Virginia starts to decrease in 2012. The highest rates for hydraulic fracturing were 3.81 wells per day in Pennsylvania at the beginning of 2012 and 0.74 per day in West Virginia at the end of 2012.

The growth rate of wells in Pennsylvania and West Virginia decreased from 2013 to 2014. The decreased growth rate of hydraulic fracturing wells may reflect the development trends of the shale gas in the Marcellus shale play in recent years due to cost of productivity and the demand for natural gas (Kerr, 2010; Sovacool, 2014). Furthermore the expensive cost of environmental remediation as water and soil contamination, health costs, and air quality, which are considered as priority issues for Marcellus Shale Formation production decisions may have contributed to the decreased the development of shale gas in this region (Coulson et al., 2011).

3.4.1.2. Total Water Volume for Wells Put into Production

The True Vertical Depth (ft.) and the Total Water Volume (gal) is shown in Figure 3-2. The data shows that no obvious linear relationship exists between these two variables, indicating that the total water volume may not depend on the vertical depth of the well. Statistical analysis of the Total Water Volume (gal) was determined to be 5,383,743 ± 2,789,077 (mean ± standard deviation, s.d.) with the median of 4,911,362, while True Vertical Depth (ft.) is 7,061 ± 1,069 with the median of 7,054. Both of the medians are close to their means, indicating both parameters of Total Volume of Water (gal) and Vertical depth (ft.) are evenly

distributed around their means. The standard deviation of the Total Water Volume (gal) is almost 58.8% of its average value, indicating great fluctuations in the Total Water Volume (gal) from well to well. The 5,071 completed wells belonged to 63 operators, and were distributed among 56 counties in Pennsylvania and West Virginia. Table 3-2 lists the counties where the wells are located and the number of wells for each county.

Flowback and produced water consists of hydraulic fracturing fluids and formation water that returns to the surface during oil or gas production (Alkhudhiri et al., 2013). Recycling or reusing the flowback or produced water as a replacement for fresh water when composing hydraulic fracturing fluids can decrease the volume of fresh water required to put a well into production. However, the various chemical species that already exist in the recycled flowback or produced waters can potentially change the chemical species and concentrations in hydraulic fracturing fluids. The actual concentrations of chemicals in hydraulic fracturing fluids may be higher or lower than the reported concentrations. Wells where the operators reported the use of recycled produced water were considered in order to account for wells where recycled produced water was used in the make-up of the hydraulic fracturing fluids, Table A-16 (in the Appendix B) lists the wells where recycled produced water was used to replace part of the fresh water. In these cases, there were 1,112 out of 5,071 wells or approximately 19.7% of the wells where recycled produced water was used.

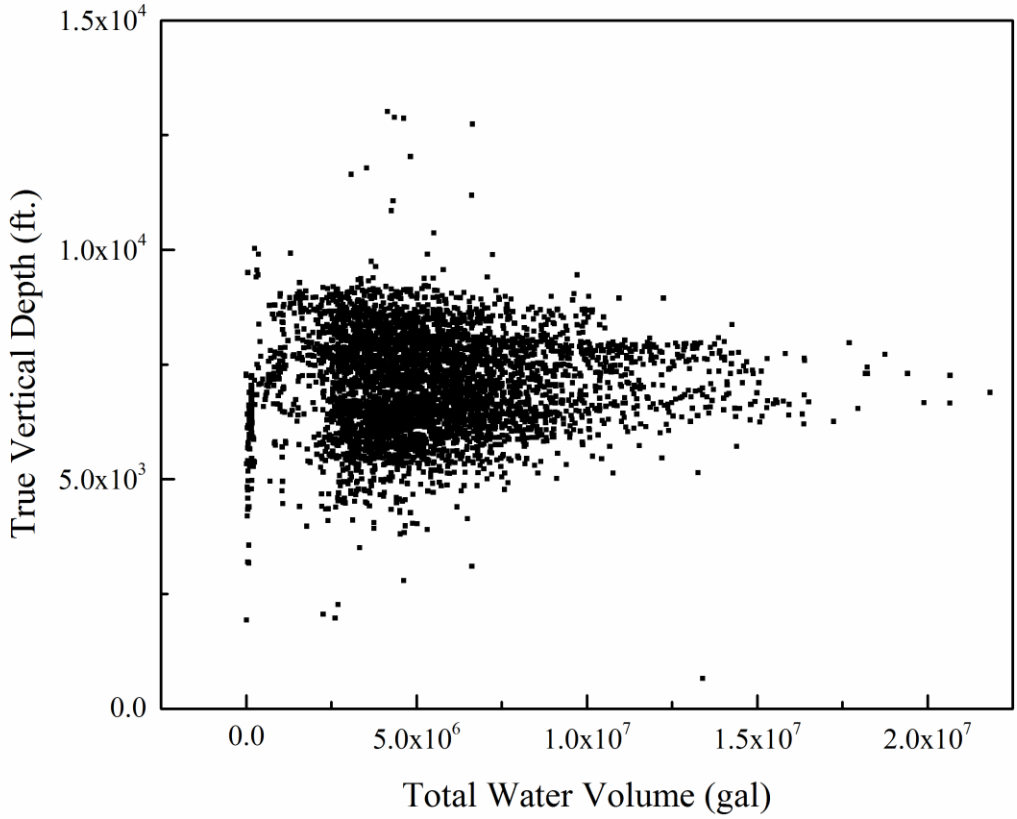

Figure 3-2. Scatter plot of total volume of water and vertical depth. There are 4,725 data points in this plot. Data in this figure is a portion of the data shown in Figure S6 in Chen and Carter (2016).

Table 3-2. Number of wells and total volume of water of each county.

County	State	Num. of Wells	Total volume of water (gal)		
			mean	minimum	maximum
Bradford	Pennsylvania	717	4,717,189	30,450	14,270,634
Susquehanna	Pennsylvania	636	5,875,016	105,840	16,390,752
Lycoming	Pennsylvania	613	4,390,193	800,250	10,530,576
Washington	Pennsylvania	504	6,081,424	254,730	19,422,270
Greene	Pennsylvania	368	6,004,366	1,144,032	18,831,536
Tioga	Pennsylvania	368	4,099,724	48,720	18,754,176
Butler	Pennsylvania	178	6,192,537	98,724	14,395,668
Westmoreland	Pennsylvania	152	5,404,275	1,778,791	16,380,966
Wyoming	Pennsylvania	141	6,701,715	855,792	13,684,524
Doddridge	West Virginia	132	7,459,679	3,183,076	13,404,355
Wetzel	West Virginia	114	5,933,392	2,595,060	10,761,231
Fayette	Pennsylvania	110	3,980,645	782,670	8,839,970
Marshall	West Virginia	106	7,995,891	2,593,046	21,833,802
Armstrong	Pennsylvania	98	2,007,901	15,078	10,384,351
Harrison	West Virginia	86	7,773,651	4,055,898	12,954,648
Ohio	West Virginia	73	6,852,548	3,310,986	14,018,172
Clearfield	Pennsylvania	63	4,757,741	80,640	11,780,874
Sullivan	Pennsylvania	62	4,671,792	430,584	9,431,184
Clinton	Pennsylvania	53	4,201,542	1,993,665	5,987,940
Taylor	West Virginia	44	5,590,719	8,519	8,470,420
Brooke	West Virginia	41	4,659,456	2,858,352	8,987,580
Mckean	Pennsylvania	38	5,527,207	153,616	9,145,332
Marion	West Virginia	38	4,588,055	1,878,072	6,936,930
Elk	Pennsylvania	37	6,299,456	3,903,690	11,383,470
Allegheny	Pennsylvania	27	4,713,051	2,286,813	8,730,291
Upshur	West Virginia	26	5,663,031	368,464	20,664,462
Beaver	Pennsylvania	25	4,930,228	299,124	13,270,033
Potter	Pennsylvania	23	4,713,317	2,191,692	6,796,778
Ritchie	West Virginia	22	7,453,722	3,680,078	12,279,605
Jefferson	Pennsylvania	21	6,313,993	155,891	11,737,479
Indiana	Pennsylvania	19	4,225,698	77,180	9,663,564
Centre	Pennsylvania	16	5,086,013	2,146,566	6,406,011
Forest	Pennsylvania	14	6,178,154	3,189,522	9,233,448
Barbour	West Virginia	14	8,743,691	2,535,162	14,049,805
Lawrence	Pennsylvania	13	5,135,268	2,419,410	14,247,085
Tyler	West Virginia	12	10,182,387	4,168,710	17,966,449
Clarion	Pennsylvania	8	4,862,300	159,935	8,644,566
Mercer	Pennsylvania	7	6,119,259	3,618,419	8,142,158
Monongalia	West Virginia	7	7,736,538	5,810,868	10,651,242
Cameron	Pennsylvania	6	6,377,712	4,871,748	8,374,926
Somerset	Pennsylvania	6	5,018,796	2,680,318	7,252,609
Venango	Pennsylvania	5	5,200,165	370,692	7,692,630
Blair	Pennsylvania	3	3,938,060	3,542,742	4,642,470
Crawford	Pennsylvania	3	3,100,262	17,250	4,803,563
Gilmer	West Virginia	3	5,330,018	13,902	8,528,341
Preston	West Virginia	3	5,613,202	5,550,888	5,721,996
Webster	West Virginia	3	1,705,774	612,738	2,259,264
Columbia	Pennsylvania	2	5,626,542	4,070,106	7,182,978
Leraysville	Pennsylvania	2	4,813,664	4,048,540	5,578,788
Warren	Pennsylvania	2	2,347,459	68,911	4,626,006
Lewis	West Virginia	2	4,920,642	4,737,978	5,103,306
Clinton / Lycoming	Pennsylvania	1	3,287,521	3,287,521	3,287,521
Huntington	Pennsylvania	1	5,325,418	5,325,418	5,325,418
Hancock	West Virginia	1	2,420,124	2,420,124	2,420,124
Pleasants	West Virginia	1	32,340	32,340	32,340
Randolph	West Virginia	1	4,291,652	4,291,652	4,291,652

3.4.2. Characteristics of Organic Species in Hydraulic Fracturing Fluids

Figure 3-3 and Figure 3-4 shows the frequency and number of wells in which different organic and inorganic compounds were used in the hydraulic fracturing fluids for the wells studied. The organic compounds were found in the 5,070 wells with a frequency of 68,555 and the inorganic compounds were added in 5,069 wells with a frequency of 25,242. The greater frequency compared to the number of wells studied is a result of the organic compounds showing up more than once in the chemical disclosure data as the chemical additive compositions may contain some of the same compounds. The organic compounds were divided into sub-groups including organics containing oxygen, which occurred in 5,062 wells and had the highest frequency of 52,181. These compounds were followed by organics containing nitrogen, sulfur, or phosphorus, which were revealed to be in 4,877 wells with a frequency of 17,575. Hydrocarbons were added in 4,256 wells with a frequency of 8,542. The following sections describe the different functional groups for the organics species and their properties that may be harmful to the environment.

3.4.2.1. Organics Containing Oxygen

Alkoxy and Ethoxy

Alkoxy group (-OR) is an alkyl group bonded to oxygen (Brown, 2013), while ethoxy group is $-OC_2H_5$. Ethoxylation adds ethylene oxide functional groups onto alcohols or phenols, forming compounds such as ethylene, propylene, and polypropylene glycols. Ethylene oxide (CAS: 107-21-1, or ethylene glycol) was found in 2,132 wells with the mean concentration of 75 ppm. Staples et al. (2001) suggested ethylene glycol is not persistent due to the rapid biodegradation under both of aerobic and anaerobic conditions after reviewing its fate and risk from previous studies. Most of the alkoxy groups observed in the reported organics is the ethoxy group (Table 3-3). More than half of organics with ethoxy groups belong to alcohol ethoxylates (AEOs), which are produced through the ethoxylation of alcohols. More than 99% AEOs can be effectively removed in wastewater treatment plants (WWTPs) (Morrall et al., 2006). Their biodegradation mechanisms are scission and then ω- or β-oxidation of the alkyl chain (Steber and Wierich, 1985), and the alkyl chain was reported to hinder anaerobic degradation (Mosche, 2004).

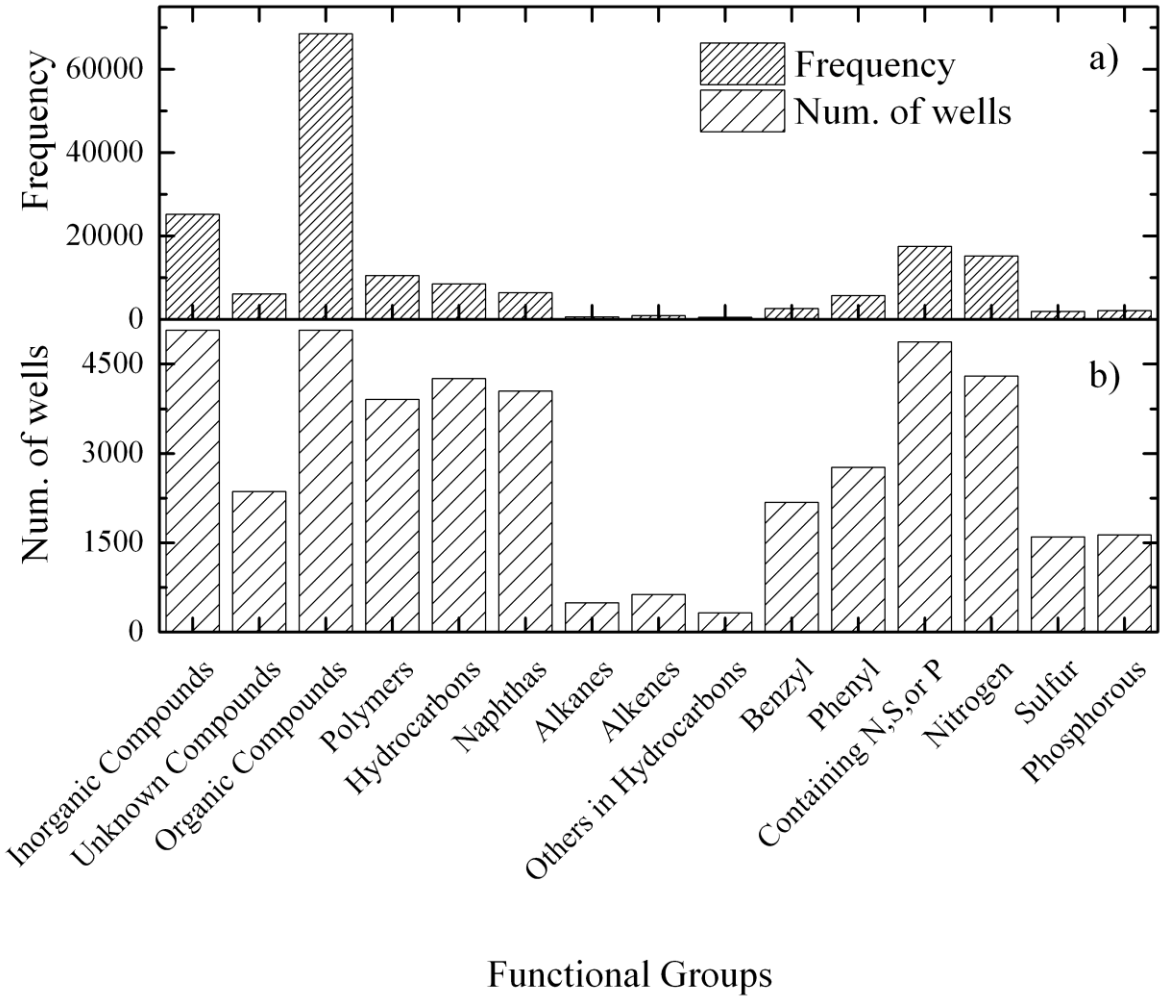

Figure 3-3. Number of wells and frequency of functional groups excepting the group of containing oxygen and its sub-groups.

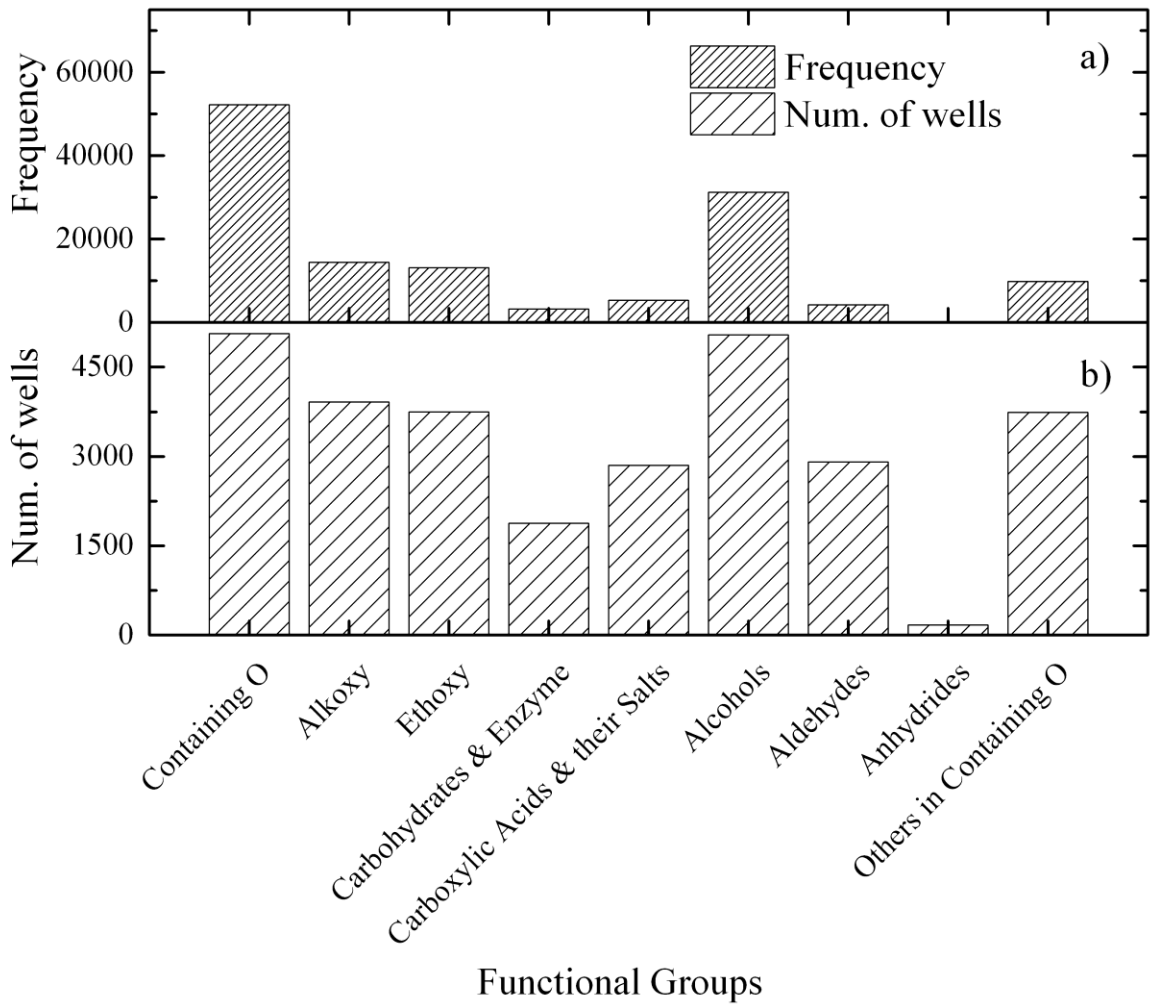

Figure 3-4. Number of wells and frequency of functional groups containing oxygen.

Table 3-3. List of Organics containing oxygen

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
Alkoxy							
polypropylene glycol	25322-69-4	78	78	1	77	7.9	0.10-148
polyoxyalkylenes	N/A	414	482	0	413	8.0	0.20-270
oxyalkylated polyamine	N/A	231	231	0	230	7.8	3.30-21
oxyalkylated fatty acid	N/A	152	152	0	152	13.1	0.10-328
aliphatic alcohol polyglycol ether	N/A	88	96	0	88	7.1	0.30-14
oxyalkylated alcohols	N/A	61	69	1	52	26.6	0.50-122
oxyalkylated phenolic resin	N/A	48	96	0	48	5.6	2.40-11
short chained glycol ether	N/A	41	41	1	40	1.8	1.10-5
oxyalkylated fatty acid derivative	N/A	39	40	0	39	68.6	1.10-630
oxyalkylated alkyl alcohols	N/A	29	29	0	28	935.1	0.30-1676
Ethoxy							
ethylene glycol	107-21-1	2132	3309	12	2094	75.0	0.01-53578
polyethylene glycol	25322-68-3	1647	1667	5	1599	131.6	0.10-4880
2-butoxyethanol	111-76-2	1300	1436	16	1251	280.1	0.02-284494
alcohols, c12-16, ethoxylated	68551-12-2	782	912	2	739	118.9	0.10-10495
octoxynol 9	68412-54-4	552	559	8	541	2.2	0.10-2110
alcohols, c14-15, ethoxylated	68951-67-7	498	501	0	494	9.4	0.20-921
diethylene glycol	111-46-6	469	469	29	411	3.8	0.05-450
ethoxylated oleylamine	26635-93-8	332	332	0	240	173	16.10-951
ethoxylated alcohol	68002-97-1	331	428	0	323	157.3	0.10-987
diethylene glycol butyl ether	112-34-5	309	309	63	239	5.0	0.01-170
alcohols, c12-14, ethoxylated	68439-50-9	220	317	0	177	187	0.10-959
alcohols, c12-14, ethoxylated propoxylated	68439-51-0	212	213	7	205	73.3	0.08-689
alkyloxypolyethyleneoxyethanol	84133-50-6	185	185	0	99	64.4	0.10-833
sorbitol tetraoleate	61723-83-9	181	181	0	95	71.1	0.10-833
polyethylene glycol monooleate	9004-96-0	181	181	0	95	74.9	0.40-833
polyethylene glycol nonylphenyl ether	9016-45-9	158	158	1	157	39.1	0.60-850
polysorbate 80	9005-65-6	108	109	0	102	21.6	0.30-921
surfactant	9043-30-5	89	89	9	80	18.1	0.10-191
4-nonylphenol branched ethoxylated	127087-87-0	71	71	0	71	0.7	0.10-500
ethoxylated branched c7-9, c8-rich alcohols	78330-19-5	67	67	0	67	0.4	0.10-10
alcohols, c9-11-iso-, c10-rich, ethoxylated	78330-20-8	67	67	0	67	0.4	0.10-10
alcohols, c9-11-iso-, c10-rich, ethoxylated propoxylated	154518-36-2	63	63	8	40	4.8	0.10-228
polyethylene glycol monohexyl ether	31726-34-8	63	63	0	63	69.3	9.00-98
1-butoxy-2-proponal	5131-66-8	59	59	0	59	30.2	0.10-191
alcohols, c11-14-iso-, c13-rich, ethoxylated	78330-21-9	52	52	0	52	3.3	0.10-41
ethoxylated propoxylated 4- nonylphenol-formaldehyde resin	30846-35-6	45	45	0	45	0.3	0.10-1
2-butoxy-1-propanol	15821-83-7	43	43	13	29	0.6	0.00-1
ethoxylated alcohols	N/A	551	608	11	512	22.4	0.01-200
aliphatic alcohols, ethoxylated	N/A	306	306	0	306	2.3	0.20-10
nonylphenol ethoxylates	N/A	145	145	2	126	7.0	0.10-18
polyethoxylated alcohol	N/A	28	35	0	28	55.7	1.60-338
Carbohydrates & Enzyme							
guar gum	9000-30-0	1642	1768	76	1528	219.1	0.01-169430
cellulase	9012-54-8	623	629	262	354	2.0	0.03-30
α-d-glucopyranoside	57-50-1	60	60	0	46	4.9	0.50-25
hemicellulase	9025-56-3	48	48	7	36	13.9	0.10-307
carbohydrates	N/A	345	349	83	257	5.1	0.10-72
polysaccharide	N/A	173	173	42	127	293	1.60-1640
vegetable gums	N/A	93	95	0	93	185.7	1.70-384
enzyme	N/A	44	45	0	39	66.9	0.20-439
cellulase enzyme	N/A	36	36	0	22	6.2	1.43-25
Carboxylic Acids & their Salts							
citric acid	77-92-9	1629	1640	11	1595	27.4	0.10-1785
acetic acid	64-19-7	718	794	1	700	85.0	0.80-1175
formic acid	64-18-6	254	259	0	253	21.2	0.02-657
fatty acids, tall-oil	61790-12-3	239	239	0	239	10.8	0.30-43
fumaric acid	110-17-8	70	70	3	67	0.7	0.10-1
sorbitan	8007-43-0	36	36	0	25	231.0	0.80-2235
fatty acids	N/A	580	580	160	415	1.2	0.10-46
aliphatic acids	N/A	323	324	1	322	2.2	0.10-10

Table 3-2. List of Organics containing oxygen (Continued)

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
fatty acid salt	N/A	173	173	159	14	0.1	0.10-0.10
fatty acids, tall oil	N/A	101	101	0	97	16.0	0.50-921
organic acid salts	N/A	29	29	0	29	61.0	54.80-74
Alcohols							
methanol	67-56-1	3328	4650	7	3272	40.7	0.00-45454
propargyl alcohol	107-19-7	3073	3157	79	2938	3.0	0.02-6480
isopropanol	67-63-0	1720	2222	11	1654	54.2	0.00-45190
ethanol	64-17-5	1258	1265	0	1172	12	0.10-133
sorbitan monooleate	1338-43-8	681	684	0	533	83.8	0.30-1090
sodium erythorbate	6381-77-7	443	444	0	443	8.5	0.30-122
propylene glycol	57-55-6	426	791	7	410	323.1	1.75-31040
2-ethyl hexanol	104-76-7	142	143	0	141	27.2	0.10-564
1-decanol	112-30-1	111	113	0	110	1.6	0.10-33
1-octanol	111-87-5	109	111	0	108	1.1	0.10-19
glycerol	56-81-5	44	45	0	44	49.4	0.10-590
aliphatic alcohol	N/A	176	176	159	17	106.6	0.10-630
alcohols	N/A	64	64	0	43	501.0	1.10-1994
Aldehydes							
glutaraldehyde	111-30-8	1843	1863	10	1811	77.5	0.80-1200
formaldehyde	50-00-0	556	556	43	444	1.2	0.03-5
Anhydrides							
acetic anhydride	108-24-7	166	183	1	163	54.7	6.50-956
Others in Organics containing O							
dioxane	123-91-1	90	90	25	65	0.1	0.10-0.30
siloxanes and silicones, di-me, reaction products with silica	67762-90-7	88	88	1	29	0.1	0.10-0.10
decamethyl cyclopentasiloxane	541-02-6	87	87	0	29	0.1	0.10-0.10
octamethylcyclotetrasiloxane	556-67-2	87	87	0	29	0.1	0.10-0.10
dodecamethylcyclohexasiloxane	540-97-6	82	82	0	26	0.1	0.10-0.10
fatty acid ester	N/A	28	29	0	28	69.6	0.10-630
polyol ester	N/A	27	27	0	27	17.6	0.40-31

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

AEOs are used as nonionic surfactants in the replacement of alkylphenol ethoxylates (APEOs) (Traverso-Soto et al., 2014). APEOs are nonionic surfactants produced by sequential addition of ethylene oxide to alkylated phenols or alkylphenols (APs) (Cruceru et al., 2012). The occurring APEOs in the hydraulic fracturing fluids were octoxynol 9 (CAS: 68412-54-4) in 552 wells with an average concentration of 2.2 ppm, polyethylene glycol nonylphenyl ether (CAS: 9016-45-9) in 158 wells with an average concentration of 39 ppm. Other less commonly observed ethoxylated compounds include 4-nonylphenol branched ethoxylated (CAS: 127087-87-0) in 71 wells with an average concentration of 0.73 ppm and nonylphenol ethoxylates (CAS: N/A) in 145 wells with an average concentration of 7.0 ppm. Though these compounds have not been observed in all wells and may not be considered toxic, the degradation intermediates of APEOs, such as short-chain APEOs and APs (*i.e.* 4-*tert*-octylphenol, and 4-nonylphenol) are considered more toxic, persistent, and estrogenic than their parent compounds (Staples et al., 2004; Huang et al., 2013; Wu et al., 2013a; Vazquez and Lo Nostro, 2014).

Both AEOs and APEOs are derived from polyethylene glycols (PEGs) (Traverso-Soto et al., 2014). The degradation of PEGs through both advanced oxidation processes (AOP) (Chiou et al., 2004; Haseneder et al., 2007; Yuan et al., 2013) and biotechnology (Otal and Lebrato, 2002; Huang et al., 2005; Bernhard et al., 2008) have been well documented. PEGs appearing in the hydraulic fracturing fluids included polyethylene glycol (CAS: 25322-68-3) in 1,647 wells with a mean concentration of 132 ppm, and 2-butoxyethanol (CAS: 111-76-2) in 1,300 wells with a mean concentration of 280 ppm. Polypropylene glycols (PPGs) are synthetic non-toxic polymers used in the formulation of copolymers with PEGs (Zgola-Grzeskowiak et al., 2007). Polypropylene glycol (CAS: 25322-69-4) appeared in 78 wells with an average concentration of 7.9 ppm. Zgola-Grzeskowiak et al. (2006) reported around 99% of both PEGs and PPGs were removed under the River Water Die-Away Test through different biodegradation pathways. Hu et al. (2007) isolated three strains (*Sphingobium sp.* strain EK-1, *Sphingopyxis macrogoltabida* strain EY-1, and *Pseudomonas* sp. Strain PE-2) which can use both PEGs and PPGs as their sole carbon source.

Carbohydrates & Enzymes

The Carbohydrates & Enzymes group includes carbohydrates, polysaccharides, or enzymes, which can be used directly as carbon sources by various microorganisms. Gums are natural, biosynthesized, or modified polysaccharides (Whistler, 2012). Vegetable gums (CAS: N/A) were observed in 93 wells with a mean concentration of 186 ppm. Guar gum (CAS: 9000-30-0) appeared in 1,642 wells with a mean concentration of 219 ppm, are polysaccharide gums extracted from trees and plants (Timar-Balazsy and Eastop, 2012). Guar gum is an environmentally friendly natural polysaccharide, and can be readily degraded by microorganisms (Gastone et al., 2014). Lester et al. (2014) reported 90% of the guar gum was removed by activated sludge after 10 hr when the total dissolved solids (TDS) was 1,500 mg/l. The removal efficiency decreased by 40% when TDS was increased to 45,000 mg/l after 31 hr of treatment time. Cellulase is a complex enzyme system for degrading cellulose, which is an abundant and water-insoluble biopolymer (Polaina and MacCabe, 2007). Cellulase (CAS: 9012-54-8) was found in 623 wells with a mean concentration of 1.96 ppm while cellulase enzyme (CAS: N/A) appeared in 36 wells with a mean concentration of 6.2 ppm.

Carboxylic Acids & their Salts

Carboxylic acids are organic compounds with the carboxyl group (-COOH). Citric acid (CAS: 77-92-9) was reported to be used in 1,629 wells with a mean concentration of 27.4 ppm. This compound is a chelating agent in the food industry and a reducing agent in photolytic and photocatalytic systems (Quici et al., 2007). Chen et al. (2013) reported 99.4% of the total organic carbon (TOC) was eliminated in a chloride photo-electrochemical process developed for mineralizing citric acid (5 mM or 961 ppm). Acetic acid (CAS: 64-19-7), found in 718 wells with the mean concentration of 85.0 ppm, is recalcitrant to oxidation due to the methyl group in α-position of the carboxyl group (Findik and Gunduz, 2007). Cihanoglu et al. (2015) found under the optimal conditions in heterogeneous Fenton-like oxidation, only 50.5% of acetic acid with the initial concentration of 100 mg/l was removed. Formic acid (CAS: 64-18-6), reported to be in 254 wells with a mean concentration of 21.2 ppm, is toxic to microorganisms and humans. Cruz Viggi et al. (2010) used non-acclimated activated sludge from a WWTP to treat formic acid, and found the removal rate

gradually decreased to zero and biodegradation activity was greatly inhibited. AOPs are considered as promising technologies for treating biologically persistent organics (Oller et al., 2011) and have been studied as a means for removing formic acid (Xiong et al., 2003; Mariani et al., 2013; Apiwong-ngarm et al., 2014).

Alcohols

Alcohols are organics with one or more hydroxyl groups (-OH) bonded to a saturated carbon. Methanol (CAS: 67-56-1), propargyl alcohol (CAS: 107-19-7), isopropanol (CAS: 67-63-0), and ethanol (CAS: 64-17-5) were the most commonly reported alcohols appearing in more than 1,000 wells as shown in Table 2. Propylene glycol (CAS: 57-55-6), aliphatic alcohol, and alcohols were found with mean concentrations higher than 100 ppm. Almost all of the added alcohols are considered to be toxic chemicals. Methanol, ethylene glycol, diethylene glycol (CAS: 111-46-6), and propylene glycol can result in alcohol-related intoxication, such as metabolic acidosis (Krautt and Kurtztt, 2008). Long-term inhalation of propargyl alcohol has been shown to raise the occurrences of respiratory/transitional epithelial adenoma in mice and rats (Thakur et al., 2013). 2-ethylhexanol (CAS: 104-76-7), found in 142 wells with a mean concentration of 27 ppm, is in the class of volatile organic compounds (VOCs) (Nalli et al., 2006), which can vaporize under normal atmospheric conditions. Short-term oral exposure to 2-ethylhexanol can induce liver peroxisome proliferation (WHO, 1993).

The alcohols frequently reported in the hydraulic fracturing fluids at high concentrations are readily removed. Biodegradation is considered to be the most inexpensive wastewater treatment technology that can remove methanol (Vallero et al., 2003; Paulo et al., 2004), ethanol (Welz et al., 2011), and propylene glycol (Delorit and Racz, 2014; Lissner et al., 2015). Biodegradation is also feasibility for isopropanol and diethylene glycol. Geng et al. (2015) found that *P. denitrificans* GH3 had the ability to utilize 90.3% of the isopropanol that was used as the sole carbon source within 7 days. Sriprapat et al. (2011) used the plant *E. cordifolius* to treat diethylene glycol contaminated water, and found that 95% of COD was reduced and no diethylene glycol remained after 12 days.

Aldehydes and Anhydrides

Aldehydes are organics with a (-CHO) functional group while anhydrides are organics with two acyl groups bonded to the same oxygen atom (R-O-R). Glutaraldehyde (CAS: 111-30-8) was reported in 1,843 wells with a mean concentration of 77.5 ppm. It is commonly used as a biocide to inhibit the growth of microorganisms, and exhibits acute toxicity toward aquatic organisms (Leung, 2001b). Although displaying a low acute dermal and inhalation toxicity to humans, it is very toxic through acute oral intake and extremely irritating to the eyes and skin (U.S. EPA, 2007). Formaldehyde (CAS: 50-00-0), reported in 556 wells with a mean concentration of 1.2 ppm, is a VOC. It is widely used as a disinfectant and was classified as "carcinogenic to humans" (Group 1) by the International Agency for Research on Cancer (IARC) (WHO, 2006). Acetic anhydride (CAS: 108-24-7), found in 166 wells with a mean concentration of 54.7 ppm, is highly corrosive and severely irritating.

Glutaraldehyde is easily degraded in wastewater through either AOPs or biotechnology. Leung (2001b) reviewed the fate and toxicity of glutaraldehyde, and found it can be easily biodegraded in water under either aerobic or anaerobic condition. Leung (2001a) also showed that glutaraldehyde tended to stay in the aquatic phase of the water-sediment system, and had a pseudo-first-order half -life of 10.6 hr and 7.7 hr under aerobic and anaerobic conditions, respectively. Kist et al. (2013) found 72.0-75.0% of the glutaraldehyde in solution was removed through the combination of O_3 with UV.

The degradation of formaldehyde has been well studied. Methylotrophic yeast *Hansenula polymorpha* can utilize formaldehyde up to 1750 mg/l in wastewater, while formaldehyde in this concentration is toxic to most microorganisms (Kaszycki et al., 2001). *Aspergillus nomius* SGFA1 and *Penicilium chrysogenum* SGFA3, isolated from untreated sewage sediments in formaldehyde-contaminated areas, degraded 3,000 and 9,000 mg/l of formaldehyde completely within 7 days, respectively (Yu et al., 2014). 96.1% of formaldehyde with an initial concentration of 1,000 mg/l was removed after 2 hours by the photocatalyst of ZnO nanoparticles, which were immobilized on glass plates (Soltani et al., 2015).

3.4.2.2. Polymers

Polyacrylamides are produced through the free radical polymerization of acrylamide. As seen from Table 3-4, polyacrylamides and acrylamide frequently appeared as components in polymers. Long chain polyacrylamide (CAS: N/A) were found in 98 wells with a mean concentration higher than 1000 ppm. Polyacrylamides are generally considered as non-toxic polymers. They can be removed through thermal, photo-, biological, chemical, and mechanical degradation, but the acrylamide monomer as a primary degradation intermediate is carcinogenic and worth noting (Caulfield et al., 2002; Lu et al., 2012). In one study, aerobic granules utilized polyacrylamides as sole carbon and nitrogen sources with a degradation rate of 2.2 mg/g MLSS • h exhibited no acrylamide monomer during the breakdown process (Liu et al., 2012). Conventional polymers would persist for a long time after disposal, and those polymers include polyethylene, polypropylene and water-soluble polymers (Gross and Kalra, 2002). These persistent polymers have also appeared in the hydraulic fracturing fluids. Cationic water-soluble polymers (CAS: N/A) have been used in the hydraulic fracturing fluids for the treatment of 162 wells with a mean concentration of 829 ppm. Biodegradable polymers are environmentally friendly materials, which can be mineralized into CO_2 and H_2O by microorganisms in the natural environments (Beach et al., 1995; Guo et al., 2012). Using biodegradable polymers to replace conventional polymers in the hydraulic fracturing fluids would be environmentally beneficial.

Table 3-4. List of Polymers.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	915	918	0	864	6.4	0.10-921
sodium polyacrylate	9003-04-7	358	358	0	358	69.0	0.50-156
poly (acrylamide-co-acrylic acid)	9003-06-9	241	243	0	224	204.0	3.90-338
anionic polyacrylamide	910644-97-2	215	215	0	124	430.9	89.60-951
acrylamide p/w acrylic acid, ammonium salt	26100-47-0	181	181	0	95	154.9	1.50-833
carboxymethyl hydroxporoyl guar blend	68130-15-4	131	138	0	130	224.5	0.10-10270
2-propenoic acid, polymer with 2 -propenamide, sodium salt	25987-30-8	110	116	0	110	290.8	4.10-13257
acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	93	93	0	93	122.8	8.00-209
poly(acrylamide and adam methyl chloride)	69418-26-4	89	89	0	78	339.8	96.20-946
polydimethylsiloxane	63148-62-9	87	87	0	83	0.1	0.10-0.20
polymer of 2-acrylamido-2-methylpropanesulfonic acid sodium salt and methyl acrylate	136793-29-8	84	84	0	84	12.8	0.90-22
2-propenoic acid, polymer with sodium phosphonate	71050-62-9	74	74	0	66	67.0	62.80-76
oxirane, 2-methyl-, polymer with oxirane, monodecyl ether	37251-67-5	73	73	2	58	4	0.10-74
poly(vinylidene chloride-co-methyl acrylate)	25038-72-6	59	59	0	59	8.9	0.10-77
polyacrylamide	9003-05-8	53	53	2	51	316.2	7.80-864
acrylic polymer	28205-96-1	48	48	0	48	39.3	27.00-45
propylene pentamer	15220-87-8	45	46	0	45	116.5	6.90-499
acrylamide sodium acrylate copolymer	25085-02-3	35	46	6	29	159.1	18.00-380
poly (acrylamide-co-acrylic acid) partial sodium salt	62649-23-4	32	33	0	29	308.1	67.00-610
polylactide resin	9051-89-2	24	29	0	24	52.6	4.70-243
anionic copolymer	N/A	222	286	0	183	43.0	4.10-4347
poly electrolyte	N/A	196	200	79	116	522.5	6.70-1219
polyacrylate	N/A	185	188	0	183	64.9	1.70-1377
alkylene oxide block polymer	N/A	172	172	8	164	0.8	0.40-2
cationic water-soluble polymer	N/A	162	165	118	44	829.2	7.30-1389
acrylamide polymer	N/A	141	141	0	141	455.5	14.80-642
neutralized polymer	N/A	135	135	0	135	88.6	11.40-141
carbohydrate polymer	N/A	131	131	0	131	382.3	2.40-2176
sodium polycarboxylate	N/A	113	113	0	106	84.5	6.90-142
aliphatic amine polymer	N/A	109	109	0	109	210.6	7.90-366
anionic polymer	N/A	107	108	0	93	55.8	3.32-395
long chain polyacrylamide	N/A	98	98	0	98	1192.2	541.40-1856
polyacrylamide copolymer	N/A	92	92	0	88	234.5	8.80-1512
acrylate phosphonate copolymer	N/A	78	78	7	71	52.9	7.60-91
polymer	N/A	78	121	8	61	647.6	0.70-1472
poly phosphonate	N/A	72	75	63	9	41.6	2.00-127
polyacrylamide polymer	N/A	68	68	0	67	324.1	142.50-480
anionic polyacrylamide	N/A	62	62	0	41	259.4	201.70-312
acrylate polymer	N/A	55	55	0	41	63.0	49.20-97
anionic polyacrylamide copolymer	N/A	39	39	0	0	N/A	N/A
acrylic polymer	N/A	33	33	0	12	115.4	113.00-120

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

Table 3-5. List of Hydrocarbons.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
Naphtha							
petroleum distillates	64742-47-8	3812	4678	11	3765	631.8	0.20-576290
naptha, hydrotreated heavy	64742-48-9	403	408	165	237	63.4	0.10-1211
naphthalene	91-20-3	144	168	19	91	0.6	0.03-34
heavy aromatic naphtha	64742-94-5	126	127	0	125	2.6	0.10-21
mineral spirits	8052-41-3	91	91	0	76	101.6	0.60-10098
distillates (petroleum), hydrotreated middle	64742-46-7	80	80	0	79	352.1	0.50-2969
petroleum distillates	64742-48-8	76	77	0	76	148.6	61.00-349
hydrotreated heavy paraffinic	64742-54-7	62	62	2	60	46.4	0.00-67
dewaxed heavy paraffinic	64742-65-0	58	58	0	58	35.0	10.00-67
solvent naphtha (petroleum)	64742-96-7	57	58	0	57	1172.3	1.00-82670
petroleum distillates	64741-68-0	54	55	0	54	3.6	0.10-24
paraffinic petroleum distillate	64742-55-8	54	54	0	54	182.1	0.70-1147
terpened and terpenoids, sweet oragne-oil	68647-72-3	50	50	0	50	1143.7	210.70-45190
light aromatic solvent	64742-95-6	41	41	0	41	1.8	0.10-24
kerosene (petroleum) hydrodesulfurized	64742-81-0	38	38	0	38	0.2	0.10-12
kerosene	8008-20-6	38	38	0	38	0.2	0.10-12
raffinates (petroleum), sorption process	64741-85-1	28	28	8	17	18.4	0.40-55
paraffinic solvent	N/A	225	231	83	141	24.7	0.70-191
petroleum distillate blend	N/A	104	104	0	97	325.3	1.80-1640
Alkanes							
alkenes, C>10 alpha-	64743-02-8	401	402	1	398	6.3	0.10-43
undecane	1120-21-4	45	46	0	45	34.2	0.80-111
tridecane	629-50-5	45	46	0	45	34.4	1.00-111
tetradecane	629-59-4	45	46	0	45	35.0	1.20-111
dodecane	112-40-3	42	42	0	42	40.9	1.50-111
cyclic alkanes	N/A	36	37	0	36	0.8	0.20-4
Alkenes							
olefins	N/A	508	805	4	470	4.4	0.10-921
n-olefins	N/A	77	77	0	62	0.6	0.20-1
Others in hydrocarbons							
aliphatic hydrocarbons	N/A	50	50	1	49	160.3	4.20-650

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

3.4.2.3. Hydrocarbons

Hydrocarbons are organics composed of only carbon and oxygen. Alkanes are saturated hydrocarbons while alkenes are categorized as unsaturated hydrocarbons (Brown, 2013). Naphtha is the liquid fraction of hydrocarbons from petroleum, which can be grouped into aliphatic and aromatic naphtha (Speight, 2006). Light naphtha boils from 30 to 90 ℃ with 5-6 carbons while heavy naphtha boils from 90 to 220 ℃ with 6-12 carbons (Speight and Arjoon, 2012). Hydrocarbons are an ideal food source for various microorganisms, and hydrocarbon-degrading bacteria have been widely reported (Rajasekar et al., 2005). Biodegradation of oil occurs mainly through degradation of aliphatic or light aromatic fractions, while the high molecular weight aromatics are recalcitrant in the environment (Leahy and Colwell, 1990). Heavy aromatic naphtha (CAS: 64742-94-5) was used in the hydraulic fracturing fluids of 126 wells with a mean concentration of 2.6 ppm. Naphthalene (CAS: 91-20-3), added in 144 wells with a mean concentration of 0.59 ppm, is one of the typical polycyclic aromatic hydrocarbons (PAHs) found in hydraulic fracturing fluids. It was classified as a possible carcinogen (Group 2B) by IARC, due to the fact that there is insufficient or inadequate evidence of its potential carcinogenic effects on animals and humans (WHO, 2002). PAHs are highly toxic and persistent in the natural environments (Wu et al., 2013b; Jing et al., 2014). Microbial degradation of naphthalene under both aerobic and anaerobic conditions has been well studied and documented.

3.4.2.4. Benzyl and Phenyl

Benzyl and phenyl groups contain $C_6H_5CH_2$- and C_6H_5-, respectively. As seen in Table 3-6, most of the organics with one or more benzene rings were placed in the benzyl group category. Three isomers of xylene, benzene, toluene, ethylbenzene, and xylene, together notoriously known as BTEX, are the most persistent gasoline compounds (Osterreicher-Cunha et al., 2009; Huang and Li, 2014). Xylene (CAS: 1330-20-7) was found in the hydraulic fracturing fluids for the treatment of 47 wells with a mean concentration of 1.6 ppm. Trimethylbenzene (TMB) includes 1,2,3-trimethylbenzene (123-TMB, CAS: 526-73-8), 1,3,5-trimethylbenzene (135-TMB, CAS: 108-67-8), and 1,2,4-trimethylbenzene (124-TMB, CAS: 95-63-6). 124-TMB and 135-TMB appeared in the hydraulic fracturing fluids with a mean concentration of 0.15 and

0.09 ppm, respectively. TMB and BTEX can be easily degraded under aerobic conditions, but both are recalcitrant under anaerobic conditions (Chen et al., 2009).

Benzalkonium chloride (CAS: 68424-85-1), found in 1,046 wells with a mean concentration of 19.5 ppm, is used as a disinfectant(Bassarab et al., 2011) and belongs to quaternary ammonium compounds (QACs). QACs contain a nitrogen atom with four attached groups and a positive charge (McMurry, 2010). Benzalkonium chloride is persistent because it tends to be adsorbed on the sludge in WWTPs and not biodegradable under anaerobic condition (Tezel and Pavlostathis, 2009). Zhang et al. (2011) found the degradation of benzalkonium chloride (mostly adsorbed on the sludge) under aerobic conditions with the initial concentrations ranged from 5 to 20 mg l^{-1} started when aqueous COD was completed consumed. AOPs are feasible technologies for degrading disinfectants or biocides, and can be further used to treat high concentration wastewater without the concern of inhibiting microbial degradation. Suchithra et al. (2015) found benzalkonium chloride (100 mg/l) was completely mineralized within 2 hours by using hybridization of activated carbon onto TiO_2.

Table 3-6. List of Benzyl and Phenyl.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
Benzyl							
benzalkonium chloride	68424-85-1	1046	1066	0	959	19.5	0.30-183
tar bases, quinoline derivs, benzyl chloride-quaternized	72480-70-7	401	401	1	400	2.2	0.10-1620
dodecylbenzenesulfonic acid	27176-87-0	257	258	12	236	0.5	0.10-40
benzyl chloride	100-44-7	156	156	54	102	0.6	0.00-11
benzene, c10-16 alkyl derivatives	68648-87-3	150	150	138	12	0.1	0.10-0.20
1,2,4 trimethylbenzene	95-63-6	90	90	0	87	0.2	0.10-12
xylene	1330-20-7	47	47	19	28	1.6	0.03-15
quaternary ammonium compounds, benzyl(hydrogenated tallow alkyl)dimethyl, stearates, salts with bentonite	121888-68-4	46	46	2	41	3.5	0.10-15
quaternary ammonium compounds chlorides derivatives	68989-00-4	45	45	0	45	0.2	0.10-0.40
1,3,5-trimethylbenzene	108-67-8	38	38	19	19	0.1	0.03-2
diethylbenzene	25340-17-4	38	38	19	19	0.1	0.03-2
Phenyl							
cinnamaldehyde	104-55-2	259	259	1	258	1.1	0.10-49
cumene	98-82-8	39	39	19	19	0.1	0.03-2
acetophenone	98-86-2	39	39	5	34	0.2	0.10-4
2-substituted aromatic amine salt	62763-89-7	38	38	0	38	0.2	0.10-12
aromatic aldehyde	N/A	611	613	16	586	3.6	0.10-328
isomeric aromatic ammonium salt	N/A	30	30	0	30	0.5	0.20-1

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

3.4.2.5. Organics Containing Nitrogen, Sulfur, or Phosphorus

Organics containing nitrogen can possibly serve as carbon and nitrogen sources to microorganisms. Choline chloride (CAS: 67-48-1), added in the fluids of 70 wells with a mean concentration of 333 ppm, is a quaternary ammonium salt. Choline is a dietary constituent and readily biodegradable (United Nations Environment Programme). 4,4-dimethyloxazolidine (CAS: 51200-87-4), a chemical component in 438 wells with a mean concentration of 146 ppm, is a severe eye irritant with relatively low acute toxicity (U.S. EPA, 1996). Dazomet (CAS: 533-74-4) appeared in the formulation for 250 wells with a mean concentration of 123.90 ppm and is a biocide and has the major degradation product of methyl isothiocyanate (CAS: 556-61-6) (Sismanoglu et al., 2004; U.S. EPA, 2008). Dazomet is considered moderately toxic through oral intake, while methyl isothiocyanate is highly toxic to fish (lowest LC_{50}=51.2 ppb) and aquatic invertebrates (lowest LC_{50}=55 ppb) (U.S. EPA, 2008). Acrylamide (CAS: 79-06-1), added to the fluids of 197 wells with a mean concentration of 1.04 ppm, is a human neurotoxin and was classified as potentially carcinogenic to humans (Group 2A) by IARC (WHO, 1986). Many isolated bacterial strains have the ability to use acrylamide as the sole carbon and nitrogen source (Jebasingh et al., 2013; Chandrashekar et al., 2014; Lakshmikandan et al., 2014).

Table 3-7. List of Organics containing Nitrogen, Sulfur, or Phosphorus.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
Nitrogen							
2,2-dibromo-3- nitrilopropionamide	10222-01-2	1774	1919	2	1748	65.8	0.10-6629
didecyl dimethyl ammonium chloride	7173-51-5	800	803	0	777	21.2	0.30-267
dimethylformamide	68-12-2	742	743	8	727	2.5	0.10-140
dibromoacetonitrile	3252-43-5	659	669	2	652	31.2	0.10-460
2-amino-2-methyl-1-propanol	124-68-5	438	438	15	423	1.7	0.40-6
4,4-dimethyloxazolidine	51200-87-4	438	438	0	438	145.5	8.80-501
3,4,4-trimethyloxazolodine	75673-43-7	438	438	10	428	9.0	4.00-137
ammonium acetate	631-61-8	331	331	0	331	30.9	0.10-78
formaldehyde amine	56652-26-7	319	319	0	319	0.9	0.80-3
dazomet	533-74-4	250	251	0	250	123.9	0.10-9699
diethanolamine	111-42-2	202	203	4	181	0.4	0.10-12
2-propenamid	79-06-1	197	197	15	106	1.0	0.10-11
methenamine	100-97-0	152	152	1	151	1632.0	0.60-56033
quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with bentonite	68953-58-2	140	140	13	98	9.9	0.10-247
trisodium nitrilotriacetate	5064-31-3	137	138	0	137	11.3	1.10-300
nitrilotriacetic acid trisodium salt monohydrate	18662-53-8	135	135	0	135	8.2	0.80-39
dimethylcocoamine, bis (chlorethyl)ether, diquaternary ammonium salt	68607-28-3	131	131	0	131	117.7	0.50-247
dimethyldiallyammonium chloride	7398-69-8	124	124	0	123	15.0	0.10-29
cocamide diethanolamine	68603-42-9	120	120	1	104	0.6	0.10-2
tetrasodium ethylenediaminetetraacetate	64-02-8	119	119	0	99	23.1	0.10-630
urea	57-13-6	92	92	0	90	8.4	0.50-51
ammonium acrylate	10604-69-0	86	86	6	41	3.1	0.10-10
ammonium, (2-hydroxyethyl) trimethyl-, chloride	67-48-1	70	70	0	70	333.4	1.50-632
ethanolamine	141-43-5	66	66	0	64	6.5	0.09-36
polyphosphoric acid, triethanolamine ester, sodium salt	68131-72-6	48	48	0	48	39.3	27.00-45
cocamidopropyl hydroxysultaine	68139-30-0	46	46	0	45	191.7	0.35-358
9-octadecenamide, n,n-bis-2 (hydroxy-ethyl)-,(z)	93-83-4	40	40	0	40	25.4	0.10-57
thiourea	62-56-6	39	39	5	34	0.1	0.10-1
diethylenetriaminepenta(methylenephosphonic acid), sodium salt	22042-96-2	35	35	0	35	20.8	2.80-25
n-methyl-n-dodecanoylglucamine	87246-72-8	30	31	7	23	4.6	0.10-12
dicoco dimethyl quaternary ammonium chloride	61789-77-3	28	28	0	28	5.7	0.60-7
2,2-dibromomalonamide	73003-80-2	27	27	24	3	0.1	0.10-0.10
quaternary ammonium compounds	N/A	760	854	17	734	12.2	0.00-296
organic amine resin salt	N/A	425	426	8	417	4.3	0.10-420
amine salts	N/A	232	232	3	227	7.8	3.30-21
amide	N/A	146	146	0	146	19.3	2.50-40
phosphoric acid ammonium salt	N/A	132	132	0	132	7.9	3.30-15
fatty acid tall oil amide	N/A	85	85	0	85	36.8	1.50-252
salt of phosphono-methylated diamine	N/A	56	56	0	56	114.4	6.20-757
sodium salt of phosphonodimethylated diamine	N/A	41	41	0	26	7.4	6.30-8
amine derivative	N/A	29	29	0	29	112.7	6.50-348
Sulfur							
2-mercaptoethyl alcohol	60-24-2	40	41	0	40	1.2	0.20-14
organic sulfur compounds	N/A	152	152	0	152	2.2	0.00-55
Phosphorous							
tributyl tetradecyl phosphonium chloride	81741-28-8	701	780	4	694	52.5	0.10-4131
triethyl phosphate	78-40-0	230	230	1	229	0.8	0.10-18
2 phosphonobutane 1,2,4 tricarboxylic acid	37971-36-1	80	80	0	50	15.6	0.14-395
2-phosphonobutane-1,2,4- tricarboxylic acid, potassium salt	93858-78-7	49	49	0	49	24.6	12.40-53
organic phosphonate	N/A	332	430	0	328	100.7	19.70-304
alkyl phosphate ether	N/A	43	43	0	42	13.7	0.10-18

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

Hexamethylenetetramine (HMT, CAS: 100-97-0), also called hexamine or urotropine, was added in the recipe for treatment of 152 wells with a mean concentration of 1,632 ppm. While HMT is chemically and biologically stable due to its cyclic symmetric structure (Hutnan et al., 2005; Middelhoven and van Doesburg, 2007), two bacteria strains isolated from soil can utilize HMT as sole carbon and nitrogen source at a low rate (Middelhoven and van Doesburg, 2007). Acidic conditions are favorable for HMT to be degraded into formaldehyde and ammonia (Hutnan et al., 2005; Taghdiri et al., 2013). ENREF_105 Hutnan et al. (2005) used an anaerobic baffled reactor (ABR) to spatially separate the phases of hydrolysis, acidogenesis, acetogenesis and methanogenesis, resulting in a pH gradient along the reactor. 96% of HMT were removed at organic loading rates of 4 kg/m^3•d and retention time of 84 hours, due to the higher hydrolysis activity under acidic conditions. Taghdiri et al. (2013) used silicotungstic acid as the catalysis, and found that more than 70% of HMT (based on TOC) was removed by H_2O_2/Fe^{2+} under the initial pH values of 1.75-2.25. Tributyl tetradecyl phosphonium chloride (CAS: 81741-28-8) was a chemical component for fracturing 701 wells with a mean concentration of 52.5 ppm, while triethyl phosphate (CAS: 78-40-0) appeared in 230 wells with 0.76 ppm. Both of these compounds were used as biocides, and little literature exists about their toxicity and degradation.

3.5. Conclusions

From September 2008 to August 2014, 4,342 and 729 wells were fractured in Pennsylvania and West Virginia. Although the number of wells increased along with time, the growth rates have decreased since 2012. The declined development of shale gas may be due to the cost of production, demand for natural gas and the environmental concerns associated with hydraulic fracturing (Kerr, 2010; Sovacool, 2014). Among the 5,071 wells used in this study, the Total Water Volume (gal) was 5,383,743 ± 2,789,077 (mean ± s.d.) with the median value of 4,911,362 and the True Vertical Depth (ft.) was 7,061 ± 1,069 with the median of 7,054. The 5,071 wells were fractured by 63 operators and throughout 56 counties in West Virginia and Pennsylvania. Of the 5.071 well, 1,112 wells reported the use of recycled produced water, which can create uncertainty in the chemical composition of the water. In the disclosures of the 5,071 wells there were 517 chemicals used to make up the different hydraulic fracturing fluids. Of the 517 chemicals, 96 were inorganic

compounds, 358 were organic compounds, and 63 could not be identified. Organics were used in the hydraulic fracturing treatment of 5,070 wells with a frequency of 68,555, while organics containing oxygen existed in 5,062 wells with a frequency of 52,181.

Many toxic chemicals have been added into the hydraulic fracturing fluids, some of which are carcinogenic or potentially carcinogenic to humans and wildlife. Furthermore, the degradation of some of these chemicals can potentially produce more toxic and persistent byproducts. Although most of the chemicals used in the hydraulic fracturing fluids can be removed when adopting the appropriate treatments, some chemicals are persistent. The persistent organics existing in hydraulic fracturing fluids increases the technological requirements of treatment processes and the cost of operations. Therefore, narrowing the number of individual chemicals used for the same purpose would enable more efficient and economic operations in treating hydraulic fracturing fluids in WWTPs before being released into the natural environments.

CHAPTER 4

POTENTIAL EMISSIONS FROM ORGANICS CHEMICAL ADDITIVES USED FOR HYDRAULIC FRACTURING FROM LIQUID STORAGE TANKS: A MODELING APPROACH

A version of this chapter are prepared for a publication:

Chen, H. and K. E. Carter (2016). "Potential Emissions from Organics Chemical Additives Used for Hydraulic Fracturing from Liquid Storage Tanks: A Modeling Approach" (submitted to *Science of Total Environment*)

Highlights

- Median emission from hydraulic fracturing wells was 0.221 kg d^{-1} per well
- Organic emissions were dominated by the non-methane volatile organic compounds
- Three organics are reported as “known to be a human carcinogen”

4.1. Abstract

Chemical additives used in hydraulic fracturing fluids are comprised of various organic compounds that are either known or potential human carcinogens. In order to estimate the emissions from these organic constituents in on-site liquid storage tanks the AP-42 model for vertical fixed roof tanks was performed on data collected from 72,023 wells in the United States put into production through hydraulic fracturing. The results showed the median daily emissions values were 0.221 kg d-1 per well on average from each well. The total annual emissions increased from 0.221 kg yr-1 in 2008 to 250,665 kg yr-1 in 2012 and were almost constant in 2013 (222,263 kg yr-1) and 2014 (250,584 kg yr-1). The non-methane volatile organic compounds (NMVOCs) affected the emissions due to the high volatility of a number of the organic contaminants in the chemical additives. There were 60 NMVOCs listed in the components of the hydraulic fracturing fluid that are on the priority list of hazardous substances defined by Agency for Toxic Substances & Disease Registry (ATSDR). These NMVOCs accounted for 95.14% of the emissions from the wells that were not due to methane release. Monte Carlo simulations indicated that the influence of the combinatorial uncertainties from the input parameters as selected by the sensitivity analysis on the annual total emissions was insignificant.

4.2. Introduction

4.2.1. Background

Hydraulic fracturing and horizontal drilling technologies allowed shale gas production to become an important energy resource in the United States (U.S.) by increasing the contact area of hydraulic fracturing with the shale formations (Barbot et al., 2013). The process of hydraulic fracturing requires large volumes of water mixed with proppants and chemical additives to be pumped into a well under high pressure. This creates fractures and openings in the shale formations allowing for the gas to be recovered (Struchtemeyer and Elshahed, 2012a; Struchtemeyer et al., 2012; Obo, 2013; Kim and Moridis, 2015). Along with the rapid development of shale gas, the negative environmental and health impacts of this technology have become a concern for many (Arthur et al., 2009; Gregory et al., 2011; Jain, 2015).

In order to make up hydraulic fracturing fluids, approximately 0.5% of various chemical additives are blended with ~99.5% water and proppants (Arthur et al., 2009; Gregory et al., 2011). Chemical additives are used in hydraulic fracturing fluids for many purposes, such as friction reducers, surfactants, scale inhibitors, biocides, and corrosion inhibitors (Arthur et al., 2009; Gregory et al., 2011; Aminto and Olson, 2012). Some of chemical additives are toxic or may form toxic byproducts, which pose adverse effects on human health (Aminto and Olson, 2012). From 2005 to 2009, U.S. House of Representatives (2011) reported that 95 products used by the hydraulic fracturing operators contained 13 different carcinogens. Stringfellow et al. (2014) found at least 5 organic compounds used in the hydraulic fracturing fluids were known or suspected carcinogens. In both reports a number of organic species were considered to be non-methane volatile organic compounds (NMVOCs) or semi-volatile organic compounds (SVOCs) that can act as the precursor for the formation of secondary organic aerosols and ground-level ozone emissions (Shao et al., 2009). Determining the quantity of air pollutants from these emissions sources is necessary for determining the exposure risks to the NMVOCs and their potential transformation byproducts.

Emission factors are beneficial for estimating the quantity of air pollutants released from various sources (Ravindra et al., 2008). Compilation of air pollutant emission factors (AP-42, Fifth Edition, Volume I) is the primary collection of air pollutant emission factors provided by the U.S. Environmental Protection

Agency (U.S. EPA) (U.S. EPA, 1995) and specifies a series of empirical models for calculating air emissions from a variety of manufacturing processes (Trumbore, 1999; Shah et al., 2006). Different AP-42 chapters provide different equations and the parameters needed to estimate the air emissions. AP-42 Chapter 4.3 (also called WATER9 software) is a model used for estimating the air emissions from the wastewater treatment plants, such as the wastewater collection, storage, and treatment systems, through the volatilization (U.S. EPA, 1998). In this equation the mass balance takes into account the physical, chemical, and biological processes (Zhang, 2010) that impact emissions into the atmosphere. The overall mass transfer coefficient, which is used to calculate the emissions rates, is estimated using the mass transfer coefficients in the gas and liquid phases under the specific systems with/without aerations, oil film layer, and the biological degradation (U.S. EPA, 1998).

AP-42 Chapter 7 utilizes the TANKS model for calculating emission rates of the organic compounds in liquid storage tanks in many industries using or producing organic liquids (U.S. EPA, 2006). The models are used to estimate the emissions rates based on the evaporation losses during storage also known as breathing losses or standing storage losses. This model takes into account the influences of temperature and pressure changes while keeping the liquid level constant (U.S. EPA, 2006). Other losses occurring during the filling and emptying operations and are also known as working losses (U.S. EPA, 2006). Previous studies have used TANKS 4.9b to estimate the emissions of VOCs from organic liquid storage tanks and found that vertical fixed-roof tanks had higher emission rates compared with externally or internally floating-roof tanks (Jackson, 2006). Other studies have used the AP-42 equations to evaluate the VOCs from vertical fixed-roof liquid tanks and it was suggested that by reducing vapor space volume and preventing high net throughput under high ambient temperature were useful ways to reduce the emissions (Lu et al., 2013).

The objective of this study was to investigate the potential emissions for the wells and organic compounds, especially VOCs and toxic organics. This study used the AP-42 equations in Chapters 4.3 and 7 to estimate the amount of emissions that are vented from a flowback pits (storage basins) and fixed-roof liquid storage tanks for the chemical additives used in the wells put into production by hydraulic fracturing.

Emissions from the open flowback pits by the AP-42 Chapter 4.3 were also calculated under the same situations described in Bloomdahl et al. (2014) for the comparisons and model validations. The model sensitivity and uncertainty analysis were carried out in order to understand the model better and estimate the biases.

4.2.2. Motivations and hypothesis

Motivations:

First motivation: compare emissions from the open flowback pits by AP-42 model and Stagnant two-film model

Second motivation: investigate the emissions of wells and organics, especially NMVOCs and toxic and even carcinogenic organics, by using the Chapter 7 in AP-42 to estimate the amounts of organics emitted from chemical additives stored in fixed-roof liquid storage tanks in hydraulic fracturing wells

Third motivation: compare emissions from the open flowback pits and the chemical storage tanks by AP-42 model

Hypotheses:

First hypothesis (H_0): AP-42 is valid compared with the Stagnant two-film model.

Second hypothesis (H_0): Organic emissions from chemical storage tanks are not important for considerations due to their quantity and toxicity.

Third hypothesis (H_0): Open flowback pits contribute higher emissions than the chemical storage tanks.

4.2.3. Summary

Conclusions about the Tested Hypotheses:

The results associated with the tested hypotheses in this Chapter are presented in Table 4-1, and the conclusions about the tested hypotheses are shown as follows:

1) The study in this Chapter do support H_0 in the first hypothesis.
2) The study in this Chapter do not support H_0 in the second hypothesis.
3) The study in this Chapter do support H_0 in the third hypothesis.

Contributions to the Overall Hypothesis and Objective:

The second motivation and the second hypothesis are contributed to the overall hypothesis and objective. The data about emissions from chemical storage tanks is necessary for calculating the air concentrations caused by chemical storage tanks and further assessing the possibility of exposure health risks. In another word, the study IV showing in the Chapter 5 is based on the emission data obtained from this Chapter.

Strengths:

1) Model validation, sensitivity analysis, and uncertainty analysis were performed.

Limitations:

1) When performing the uncertainty analysis, five input parameters (I, T_{AX}, T_{AN}, a, H_L/H_S) were without the know distributions and the uniform distributions were assumed.
2) Meteorological data (I, T_{AX}, T_{AN}) was obtained from the nearest observation stations from the wells, and was not the field data at the exact location of wells.

Table 4-1 Results related with the hypotheses

Hypotheses	Results related with the hypothesis
First hypothesis	• The ratio of emissions estimated using the AP-42 Chapter 4.3 to those established using the stagnant two-film model ranged from 0.98 and 1.22, with a median value of 1.11. • The emissions from those two models are comparable under the considered situations, and emissions from the AP-42 Chapter 4.3 is be expected to be around 11% higher than those from the stagnant two-film model.
Second hypothesis	• For wells that were fractured over one day or more, the median value in average daily emissions for each well was 0.221 kg d^{-1} in all 14 states used in this study. • The total annual emissions increased greatly from 0.221 kg yr^{-1} in 2008 to 250,665 kg yr^{-1} in 2012 and were almost constant in 2013 (222,263 kg yr^{-1}) and 2014 (250,584 kg yr^{-1}). More than 90% of the total annual emissions were composed of the volatilization of NMVOCs and rose continuously from 0.221 kg yr^{-1} in 2008 to 237,911 kg yr^{-1} in 2012. • 95.14% of NMVOC emissions was caused by 60 compounds, which belong to the 2011 ATSDR list of candidate substances. 16.73% of NMVOCs emission was produced by 15 NMVOCs which were listed in the 13th Report on Carcinogens (NTP, 2014).
Third hypothesis	• The mean emissions per well from the open flowback pits calculated using the AP-42, Chapter 4.3 was 0.166 kg d^{-1} for the total xylenes, 0.110 kg d^{-1} for toluene, 0.061 kg d^{-1} for benzene, and 0.021 kg d^{-1} for ethylbenzene. • The mean emissions per well for the total xylenes, toluene, benzene, and ethylbenzene were 0.013, 0.024, 0.113, and 0.014 kg d^{-1}, respectively, and were calculated from the AP-42 Chapter 7 equation for the storage tanks.

Future Directions:

1) The results and conclusions in our study are based on the modeling data. Therefore, the field data would make those conclusions more valid.

2) Monitor the field meteorological in the hydraulic fracturing wells which will make the modeling results more accurate

4.3. Methodology

4.3.1. Data Collection and Screening

4.3.1.1. Hydraulic Fracturing Wells

The well data in this study was obtained from the website www.FracFocus.org (FracFocus, 2015), and was described in detail in Chen and Carter (2016). MATLAB version R2015a (The MathWorks, Natick, MA) with Statistics Toolbox was employed to import and analyze the data. Since most of the data was unavailable for the variable of Max Additive Concentration (%), the chemical concentrations in the chemical additives (C_{ca}) and volumes of chemical additives (V_{ca}) were calculated according to Equation A-2 and Equation A-3 in the Appendix C. There were 80,164 wells in the database, 44,607 of these wells reported both the fracturing start and end dates. Of the 80,164 wells there were 35,557 that reported only one date, which was considered to be the fracturing start date. Using Equation A-4 and Table A-17 (in the Appendix C), a weighted fracturing day (t_{wfd}) of 4 days was calculated and assigned as the number of fracturing days (t_{fd}) for the 35,557 wells. The requirements for the AP-42 calculations include the following: (1) well were fractured between 2008 and 2014, (2) all wells were located in the US in order to obtain the necessary meteorological data, (3) the amount of water used was reported for each well, and (4) the chemical concentration for each component and the volume percent must be greater than zero.

Based on the reported coordinates there were 79,963 wells located in the U.S., while the data for 79,957 wells disclosed the amount of water used. There were 79,603 wells disclosures that included the total chemical concentration and volume percent of the chemicals in the hydraulic fracturing fluids. In all there were 79,095 wells where all four requirements used for this study were met. However, after further analysis the number of wells decreased to 75,486, as the majority of the wells were fractured within 14 days. However, based on the fourth criteria 72,023 were chosen for this study as the organic chemicals were reported in their hydraulic fracturing fluids while the other wells only reported the inorganic species or organic species without known physical/chemical properties (Table A-18 found in the Appendix C).

4.3.1.2. Physical/Chemical Property

Estimation programs interface (EPI Suite™, U.S. EPA), comprising of more than a dozen individual models, was used for estimating physical and chemical properties of various chemical constituents (U.S. EPA, 2015). Over 2,302 individual chemicals added to the various additives making up the hydraulic fracturing fluids, however; only 1,169 of these chemicals had associated CAS Registry Numbers (CASRN). Of the 1,169, there were 693 chemicals with properties that matched those found in the EPI Suite™ software. Further inspection showed that 475 organic species reported in the 72,023 well used for this study had emissions data available for use in this study.

Based on the data provided, the chemicals were divided into two groups volatile organic compounds (VOCs), which have boiling points less than or equal to 250 °C at 101.3 kPa, and non-volatile organic compounds (NVOCs) (The European Parliament and the Council of the European Union, 2004). According to these criteria there were 175 VOCs and 300 non-volatile organic compounds (NVOCs). The 175 VOCs were referred to as non-methane volatile organic compounds (NMVOCs) since this study was used to investigate the non-methane emissions. MPBPWIN™ (a chemical property model in EPI Suite) was used to obtain the melting points, boiling points, and vapor pressures from -40 °C to 50 °C with an interval of 2 °C. The Antoine and Modified Grain equations (Equation A-6 and Equation A-3, respectively, in the Appendix C) were regressed using the vapor pressures obtained from EPI Suite and MPBPWIN (Mackay and Boethling, 2000).

4.3.1.3. Lists of Chemical Substances

The 2011 priority substance list was downloaded (on June 11, 2015) from the Agency for Toxic Substances & Disease Registry (ATSDR). There are 847 substances on the priority substance list, which were scored and ranked by ATSDR according to their frequency, toxicity, and potential for human exposure in subcategories of concentration and exposure. The top 275 ranked substances were considered the Priority List of Hazardous Substances (ATSDR, 2013).

Information for the substances listed in the 13th report on carcinogens released by the U.S. Department of Health and Human Services (NTP, 2014) was downloaded from the National Toxicology Program. There

were 267 listed substances, 226 of which were reported with CASRN. The chemical inventory published by the U.S. EPA and the Toxic Substances Control Act (TSCA) was also downloaded. This list contained 67,452 chemicals that were manufactured or processed in or imported into the U.S. without the exemptions under the TSCA.

4.3.1.4. Temperature and Solar Radiation

The data for daily maximum ambient temperature (T_{AX}) and daily minimum ambient temperature (T_{AN}) from 2008 to 2014 were obtained from over 3,965 observation stations located in 14 states. The data was provided by National Centers for Environmental Information (NCEI), which is part of the National Oceanic and Atmospheric Administration (NOAA). The data for hourly solar radiation received on a horizontal surface (Wh/m^2) from 2008 to 2010 were found in 469 observation stations and were provided by National Solar Radiation (NSR). This data was used to calculate daily total solar insolation on a horizontal surface (I). The distances from the nearest station to each well are shown in Table A-19 (in the Appendix C). The median distances from wells to the nearest temperature and solar radiation stations are 12.16 and 29.50 miles, respectively.

4.3.2. Descriptions of AP-42 and Case Study Scenario

The AP-42 model for vertical fixed-roof tanks was input into MATLAB. The description of variables and equations are shown in Table A-20 and Table A-21 in the Appendix C. The input parameters were separated into the following three groups: meteorology, tanks, and chemicals (Table A-22 in the Appendix C). Tank paint solar absorption (a) for various paint colors and types is shown in the model's manual. When specific information is not available, 0.17 is suggested for the most common or typical tank surface used (U.S. EPA, 2006). Intermediate bulk containers are commonly used as chemical storage tanks in hydraulic fracturing (shown in Figure 1-3), and their dimensions are summarized in Table A-23 (in the Appendix C). Since the tank data was not available in this study, the dimensions of chemical storage tanks were assumed as 1.22 × 1.02 × 1.35 m (Length × Width × Height) and the ratio of the maximum liquid height (H_L) to the tank height (H_S) was assumed as 0.75, which induces some uncertainty into the calculations (Table A-23 in the Appendix C). Pure vapor pressure (P) was acquired by using daily average liquid surface temperature

(T_{LA}) to solve the fitted equations regressed with the pure vapor pressure obtained from EPI Suite™. Pure vapor pressure was calculated using the average of the Antoine and Grain-Watson estimates for liquids and the Modified Grain estimate for solids (U.S. EPA, 2015). The partial vapor pressure (P_i), for each chemical, was obtained by multiplying P by the mole fraction of the chemical (x_i). The daily on-site storage volume ($V_{j,\ s}$) and daily consumption volume ($V_{j,\ w}$) was calculated from V_{ca} and t_{fd} (Equation A-8 and Equation A-9 in the Appendix C). In order to estimate the emissions, the following was assumed: 1) chemical additives were evenly mixed and stored *on-site* in vertical fixed-roof storage tanks; 2) all the chemical additives were transported to sites at the beginning of hydraulic fracturing and there was no transportation during hydraulic fracturing; and 3) the chemical additives stored *on-site* were completely consumed at the end of hydraulic fracturing.

AP-42 Chapter 4.3 (also called WATER9 software) (U.S. EPA, 1998) was used to calculate the emissions from the open flowback pits under similar situations as those described in Bloomdahl et al. (2014). The equations used in this study are shown in Table A-24 and Table A-25 in the Appendix C under the assumptions: 1) no aeration, 2) no oil film layer, 3) no biologically active, and 4) disposal instead of flow through. Those assumptions fits the situations described in Bloomdahl et al. (2014). The input data in the AP-42 Chapter 4.3 which were taken from Bloomdahl et al. (2014), included: the concentrations of 12 VOCs in the open flowback pits, the size of the open flowback pits (125 ft wide by 125 ft long by 8 ft deep), the temperature (25 °C), the air velocity (4.47 m s^{-1}), and the physical properties of 12 VOCs (diffusivity in water and air). Henry's law constants of 11 VOCs were obtained from the AP-42 Chapter 4 Section 3 (U.S. EPA, 1998), and the Henry's law constant of carbon tetrachloride was found in Toxicological and Health Professionals provided by ATSDR on May, 3rd, 2016. The Henry's law constants of 12 VOCs listed in Bloomdahl et al. (2014) and were converted to reflect the units of the Henry's law constants in the AP-42 equation (U.S. EPA, 1998).

4.3.3. Sensitivity and Uncertainty Analysis

Model sensitivity analysis was performed to investigate the effect of the input parameters on the emission from each of the organic compounds if presented in their pure form. The method was revised from

Mattioli et al. (2015) and the 25th, 50th, and 75th percentiles of each parameter are shown in Table A-26 in the Appendix C. After setting each input parameter at the 50th percentile, the output from the model was considered as p75 when setting one input parameter to its 75th percentile, and as p25 when setting the same input parameter to its 25th percentile. The absolute value of the log of p75/p25 was used to evaluate the sensitivity. When the index of abs($\log_{10}$(p75:p25)) is equal to 0 it is implied that the emissions are not affected by the input parameter. The higher the value for the abs($\log_{10}$(p75:p25)), the more sensitive the emissions are to the input parameter.

Monte Carlo simulations consisting of 10,000 runs were applied to quantify the effect of the uncertainties from the input parameters, as determined by sensitivity analysis, on the annual emissions of 72,023 wells. Besides t_{fd}, the selected parameters of I, T_{AX}, T_{AN}, a, H_L/H_S were considered as being uniformly distributed in the range of 90% and 110% of their values. For the parameter of t_{fd}, the integer value from 1 to 14 was randomly assigned as t_{fd} in each simulation. The frequency of each integer was equal to its corresponding frequency in 40,937 wells, which reported the fracturing start and end dates and were fractured within 14 days (Table A-27 in the Appendix C). The uncertainty from t_{fd} was performed on the wells that only reported the fracturing start date. For wells with both the fracturing start and end dates reported, their reported t_{fd} were used.

4.4. Results and Discussion

4.4.1. Emission Characteristics of Wells

4.4.1.1. State-level Well Emissions

The emissions for the wells are shown in Figure 4-1 (and Figure A-12). For wells that were fractured over one day or more, the median value in average daily emissions for each well was 0.221 kg d^{-1} in all 14 states (Figure 4-1) used in this study. The largest median emission value was 0.507 kg d^{-1} occurring in North Dakota. This was followed by 0.395 kg d^{-1} and 0.329 kg d^{-1} in New Mexico and Texas, respectively. The states with the lowest median emissions values were 0.001 kg d^{-1} in California, followed by 0.047 kg d^{-1} in Pennsylvania, 0.048 kg d^{-1} in Wyoming, 0.070 kg d^{-1} in West Virginia, and 0.084 kg d^{-1} in Colorado. The 10th percentiles of 9.95×10^{-5} kg d^{-1} in California were extremely small compared to the 10th percentiles

in other states. It deserves to mention that the mean emission in each state was much higher than the median emission (Figure 4-1), due to the existing of high-emitting wells (Zavala-Araiza et al., 2015). Controlling the emissions in those wells would be greatly beneficial for organic emission reductions.

Median emission values in states were comparable with the reported emissions from other contaminant sources, such as industrial landfill (Gallego et al., 2014) and municipal solid waste plant (Kim et al., 1995). For example, Gallego et al. (2014) estimated the emission of 60 VOCs in a closed industrial landfill to be 77 ± 17, 237 ± 48, and 222 ± 46 g d^{-1} using the Kriging, Global, and Tributary area methods, respectively. Kim et al. (1995) estimated that the average emission of 9 VOCs from a municipal solid waste co-composting facility to the atmosphere was around 111 g d^{-1}. Yang and Chen (2004) calculated the emissions of 21 polycyclic aromatic hydrocarbons (PAHs) from various emissions sources and found them to range from 0.06 to 28.5 kg d^{-1} depending on the source.

4.4.1.2. Annual Total Emissions

Figure 4-2 shows the total annual emissions for NMVOCs and NVOCs from 2008 to 2014. The total annual emissions increased greatly from 0.221 kg yr^{-1} in 2008 to 250,665 kg yr^{-1} in 2012 and were almost constant in 2013 (222,263 kg yr^{-1}) and 2014 (250,584 kg yr^{-1}). More than 90% of the total annual emissions were composed of the volatilization of NMVOCs and rose continuously from 0.221 kg yr^{-1} in 2008 to 237,911 kg yr^{-1} in 2012. Again the emissions remained constant with 208,607 kg yr^{-1} in 2013 and 241,702 kg yr^{-1} in 2014. The increasing trend exhibited by in these emissions follow the increase in the number of wells fractured annually, which went from 2 in 2008 to 21,906 in 2013. In 2014 the number of well fractured decreased to 20,177 in 2014.

The annual well emissions and volume of chemical additives are shown in Figure 4-3 and Figure A-13. According to these figures, the tendency of the well emissions was to fluctuate; however, the overall trend actually increased. The median value in well emissions from each well was 0.110 kg in 2008 and 0.786 kg in 2014 (Figure A-13). Except the lowest value of 0.007 kg m^{-3} per well in 2008, the median value in well emissions normalized by the volume of chemical additives was 0.015 kg m^{-3} per well in 2010 and 0.026 kg m^{-3} per well in 2009 without the obvious increasing or decreasing tendency (Figure 4-3.a). In Figure 4-3.b,

the median amount of chemical additives, in volume, decreased from 8,333 m^3 per well in 2008 to 5,031 m^3 per well in 2009 and then continuously increased over the next 5 years to 14,151 m^3 per well by 2014. The increasing trend in the volume of chemical additives, instead of the amount of emissions per cubic meter of chemical additives, may be on reason for the increasing emissions from each well. Well emissions from the storage tanks used to store the chemical additives in this study were much lower than the hydraulic fracturing emissions reported by the previously mentioned studies.

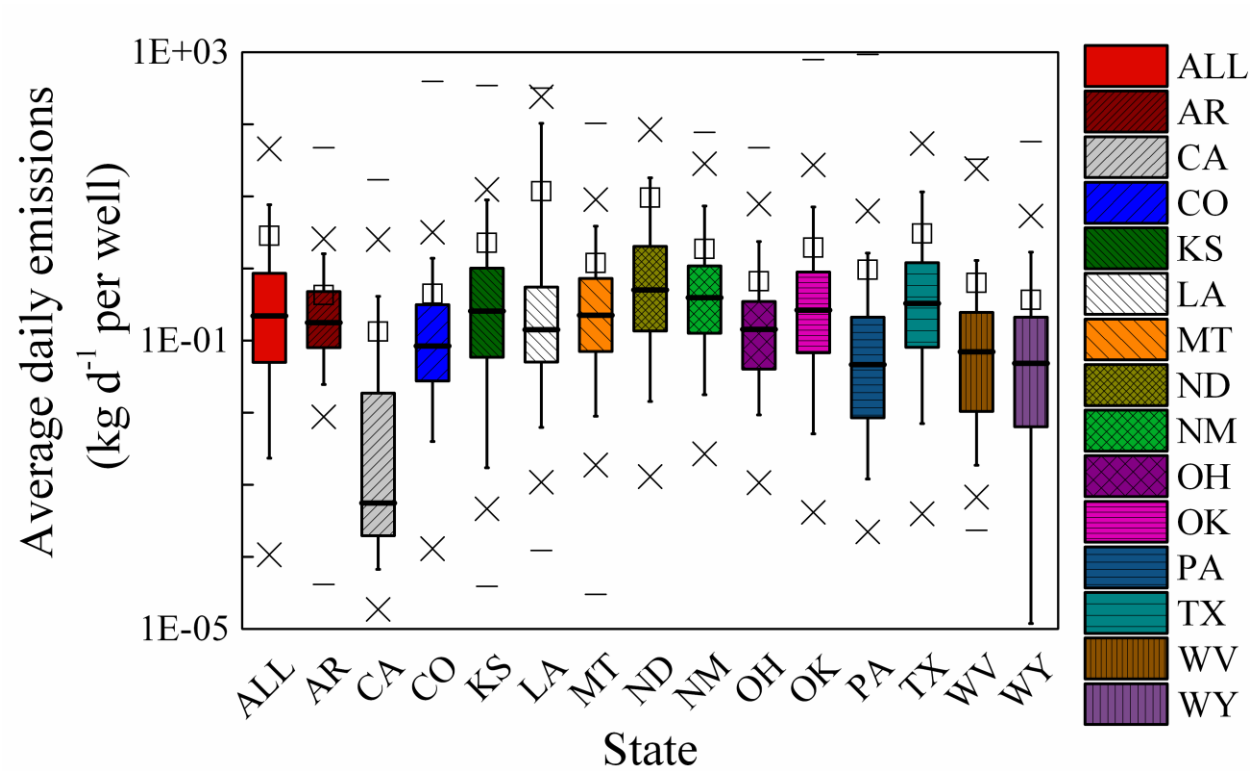

Figure 4-1. The average daily emissions per well per day (kg d^{-1} per well) are shown for each state. Horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles while whiskers denote the 5th and 95th percentiles. Open squares (□) indicate the mean value. The lower (×) and upper (×) are 1th and 99th percentiles, respectively. The lower (-) and upper (-) are maximum and minimum values.

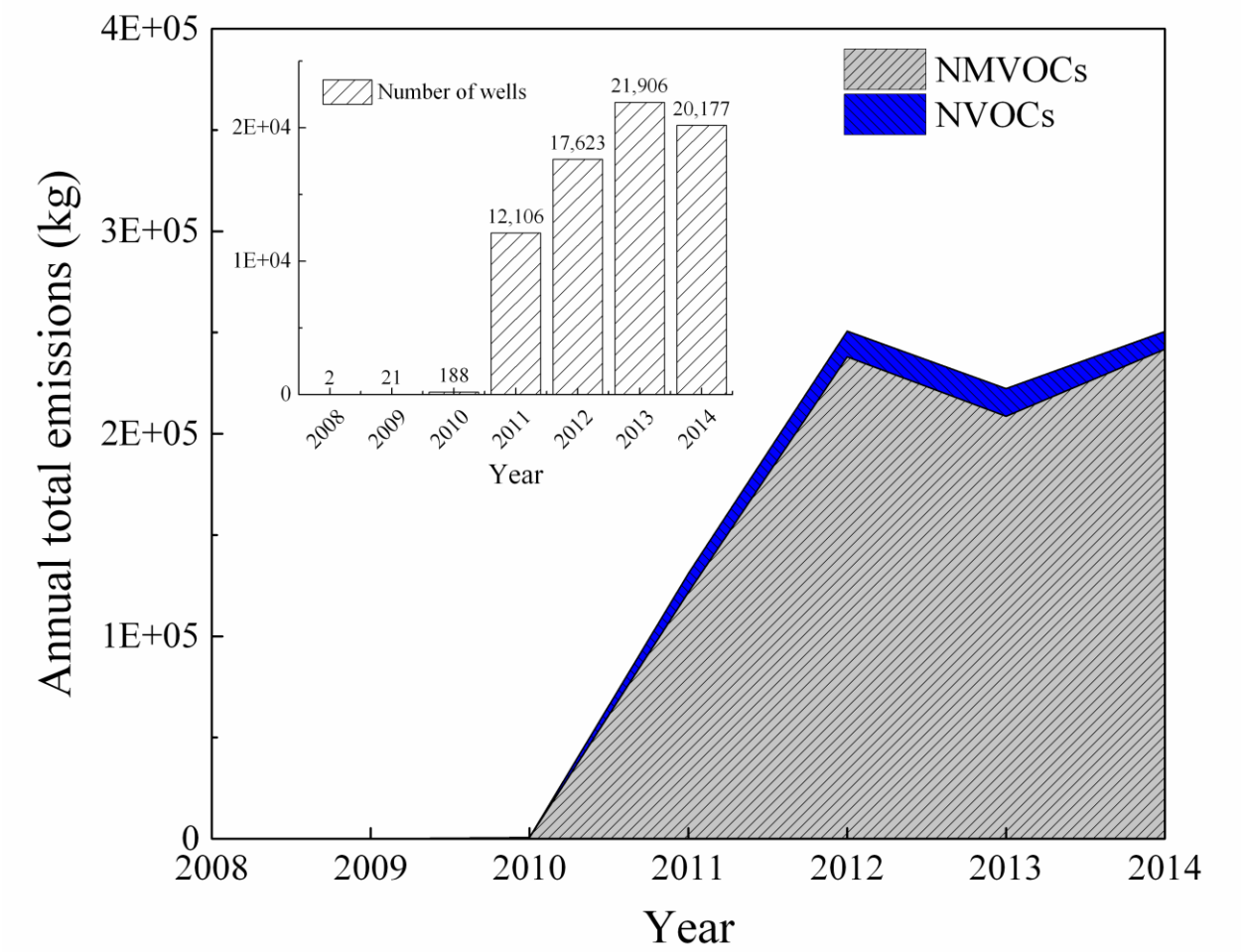

Figure 4-2. Total annual emissions for NMVOCs and NVOCs from 2008 to 2014. The inlayed plot indicates the number of wells put into production from2008 to 2014. Graph shows that as the number of wells increased, the emissions also increased for both the NMVOCs and NVOCs.

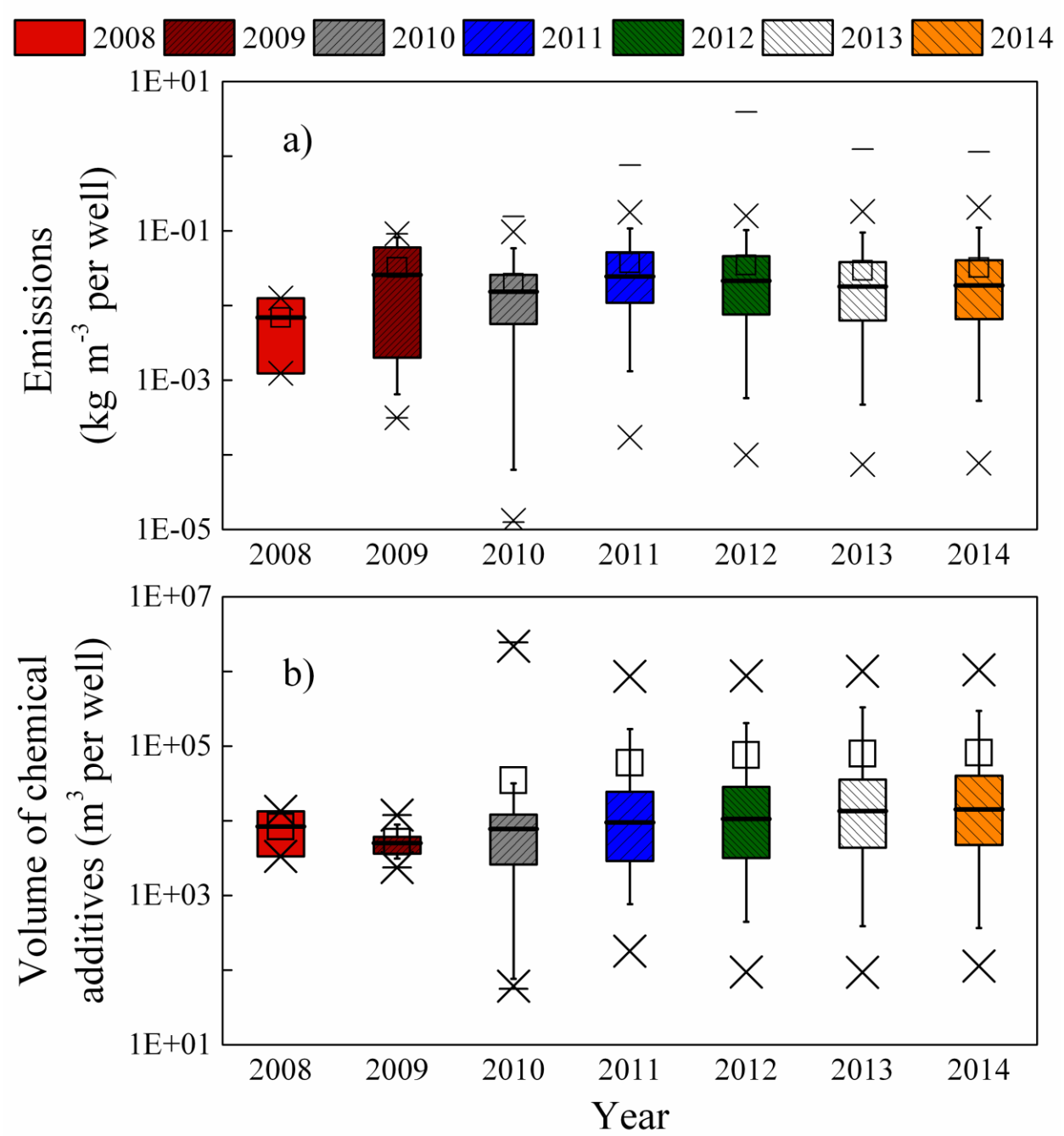

Figure 4-3. Time series analysis for the well emissions a) chemical additive emissions in each well (kg m^{-3}) and b) volume of chemical additives in each well (m^3) are shown. Horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles while whiskers denote the 5th and 95th percentiles. Open squares (□) indicate the mean value. The lower (×) and upper (×) are 1th and 99th percentiles, respectively. The lower (-) and upper (-) are maximum and minimum values.

4.4.2. Emission from the Organic Compounds

4.4.2.1. State-level Organic Emissions

Figure 4-4 (and Figure A-14) illustrates emissions of organic species in the chemical storage tanks, which were closely related with the well emissions. Each data sample in Figure 4-4.a represents the median emission of an organic, and the total emissions of each organic are shown in Figure 4-4.b. In Figure 4-4.a, the 50th percentile of median organic emissions was 3.48×10^{-9} kg d^{-1} per well. The highest value in the 50th percentiles was 5.64×10^{-7} kg d^{-1} per well in Ohio, followed by 2.71×10^{-7} kg d^{-1} per well in Arkansas, 1.98×10^{-7} kg d^{-1} per well in Pennsylvania, and 1.17×10^{-7} kg d^{-1} per well in West Virginia. The smallest values in the 50th percentile was 4.37×10^{-9} kg d^{-1} per well in Colorado, followed by 7.24×10^{-9} kg d^{-1} per well in Montana, 7.31×10^{-9} kg d^{-1} per well in North Dakota, and 7.84×10^{-9} kg d^{-1} per well in New Mexico. The 50th percentiles ranged from 1.33×10^{-8} kg d^{-1} per well to 9.81×10^{-8} kg d^{-1} per well in Wyoming, Texas, California, Oklahoma, Louisiana, and Kansas. Median organic emissions from chemical additives were very low compared with those from other contaminant sources from the storage tanks for the chemical additive. Emission factors of benzene (CARN: 71-43-2), toluene (CARN: 108-88-3), ethylbenzene (CARN: 100-41-4), and xylenes (CARN: 1330-20-7) in petrochemical wastewater from wastewater treatment plants (WWTPs) were estimated as 782.74, 86.40, 115.78, and 3.65 kg d^{-1}, respectively, by U.S. EPA WATER9 (Fatehifar et al., 2008).

In Figure 4-4.b, the 50th percentile of total organic emissions was 3.64×10^{-6} kg. The lowest and highest values in the 50th percentiles were 1.03×10^{-6} kg in California and 1.01×10^{-4} kg in Pennsylvania. The ratios between the highest and lowest values in the 50th percentiles were 128.92 kg d^{-1} per well and 97.77 kg were for median organic emissions and total organic emissions, respectively. This indicates the organic emissions varied greatly among the states. In addition, the 25th and 75th percentiles in every box in Figure 4-4 and Figure A-14 differed greatly due to the varied emissions among organics in a single state. As shown in Figure A-15, the 50th percentiles for the median organic emissions and the total emissions were positively dependent on the number percentage of NMVOCs, and negatively related with the number percentage of NVOCs.

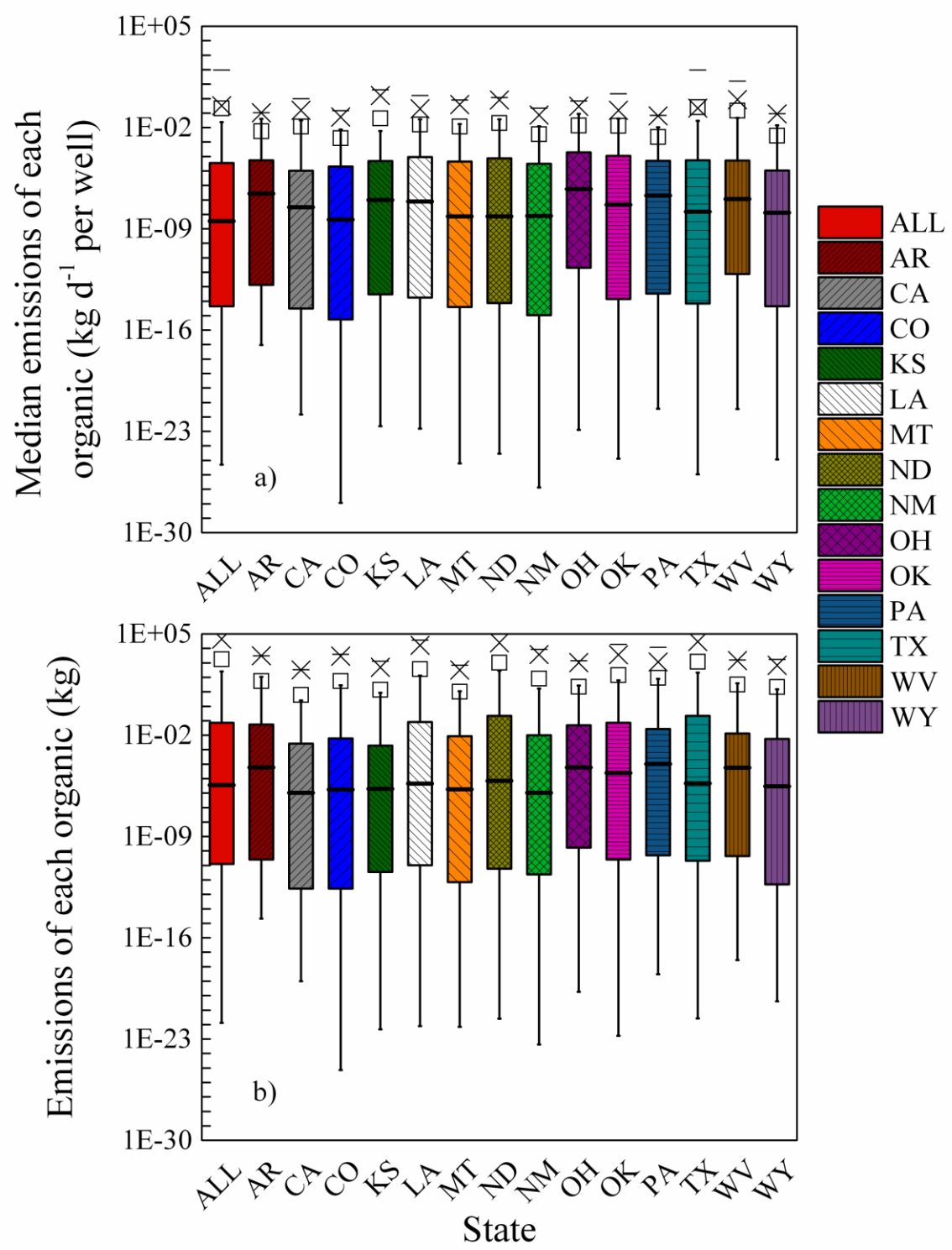

Figure 4-4. Organic compound emissions found in each well put into production: a) median emissions of each organic in each well (kg d^{-1}) and b) emissions of each organic in all wells (kg) studied. Horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles, while whiskers denote the 5th and 95th percentiles. Open squares (□) indicate the mean values. The lower (×) and upper (×) represent the 1th and 99th percentiles, respectively. The lower (-) and upper (-) are maximum and minimum values.

4.4.2.2. Emissions of NMVOCs and NVOCs

Figure 4-5 (and Figure A-16) shows the NMVOCs and NVOCs emissions for the wells put into production. The 50th percentile of median emissions for NMVOCs and NVOCs was 9.19×10^{-5} and 1.40×10^{-13} kg d^{-1} per well, respectively and are shown in Figure 4-5.a. Since NMVOCs and NVOCs were mixed evenly and stored together *on-site*, they should have similar values in the operational parameters, such as T_{LA}, which is shown in Figure 4-5.b. The 50th percentile of the median T_{LA}s for NMVOCs and NVOCs was 19.79 and 20.36 °C, respectively. The median concentrations (in %) for each organic compound are shown in Figure 4-6 and the 50th percentile of the percent of these organic compounds in the storage tanks were 0.166% for NMVOCs and 0.154% for NVOCs. The data from Figures 5 and 6 indicates that the emissions from chemical additives stored on-site were significantly dominated by NMVOCs, which is a function of the high volatility exhibited by the compounds.

Figure A-17 shows the number of NMVOCs and NVOCs according to the TSCA, ATSDR and the US Department of Health and Human Services. It was determined that there were 141 organics with unknown or variable compositions, complex reaction products and/or biological materials or UVCB (shown in Table A-28 in the Appendix C). UVCB is a chemical inventory group used by the TSCA to describe liquid hydrocarbon fractions, which are largely produced by the distillation of petroleum (McKee et al., 2015). Due to their complex and variable compositions, it is still a challenge to categorize the hazardous effects of UVCB substances (Clark et al., 2013). In this study there were 107 organics out of 141 with boiling points higher than 250 °C. However, 63 organics of the 141 have Henry's law constants greater than 10^{-5} atm m^3 mol^{-1} at 25 °C and can quickly evaporate in dilute water solutions. In Figure A-17.b, 95.14% of NMVOC emissions was caused by 60 compounds, which belong to the 2011 ATSDR list of candidate substances. In Figure A-17.c, 16.73% of NMVOCs emission was produced by 15 NMVOCs which were listed in the 13th Report on Carcinogens (NTP, 2014).

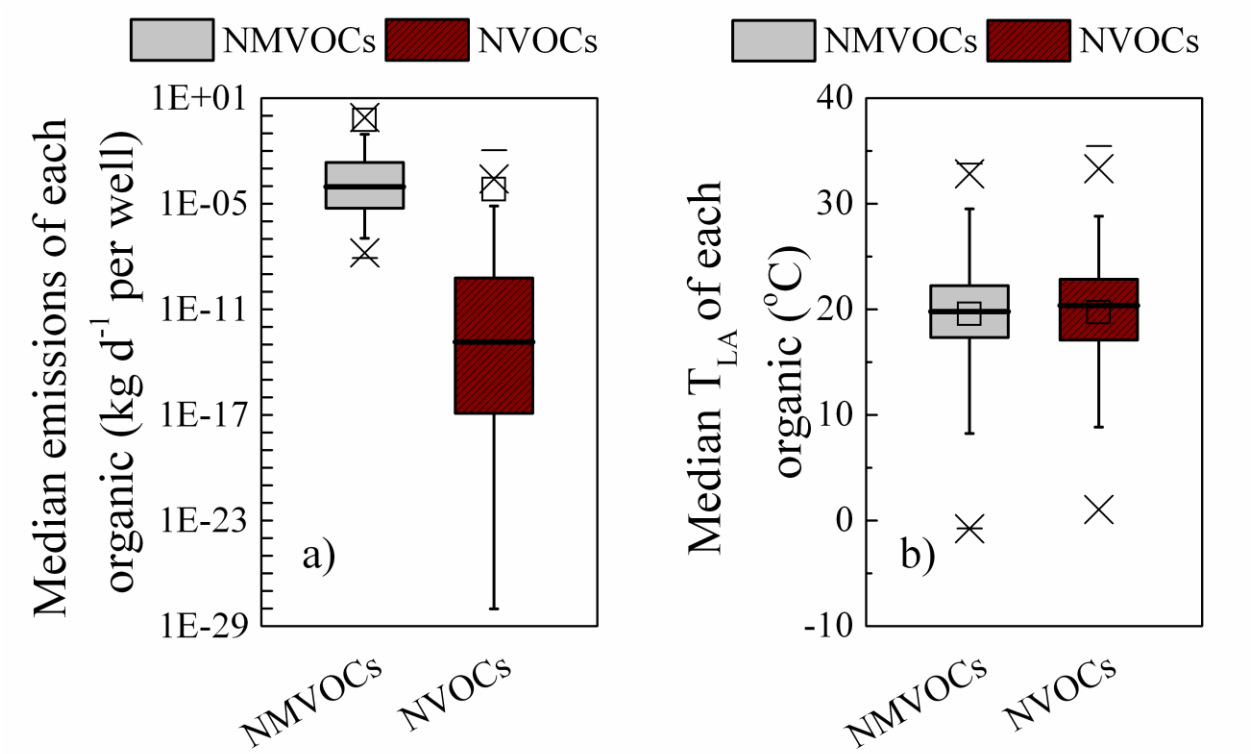

Figure 4-5. NMVOCs and NVOCs emissions for each well: a) median emissions of each organic (kg d^{-1} per well) and b) median values for daily average liquid surface temperature (T_{LA}) (°C) for each organic compound. Each data sample represents the corresponding median value of an organic. Horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles while whiskers denote the 5th and 95th percentiles. Open squares (□) indicate the mean value. The lower (×) and upper (×) are 1th and 99th percentiles, respectively. The lower (-) and upper (-) are maximum and minimum values.

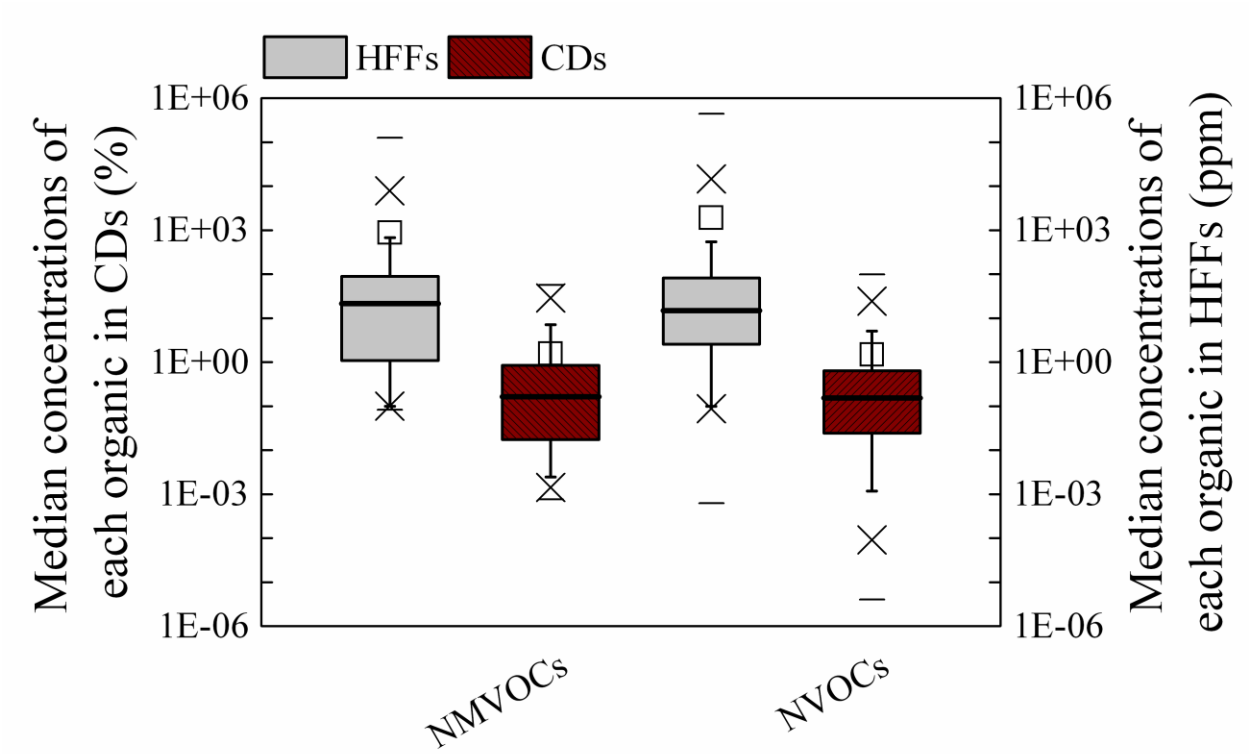

Figure 4-6. NMVOCs and NVOCs concentrations for each well: median concentrations of each organic compound in hydraulic fracturing fluids (ppm) and in the chemical additives (%). Each data sample represents the corresponding median value of an organic. (CDs: chemical additives; HFFs: hydraulic fracturing fluids.) Horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles while whiskers denote the 5th and 95th percentiles. Open squares (□) indicate the mean value. The lower (×) and upper (×) are 1th and 99th percentiles, respectively. The lower (-) and upper (-) are maximum and minimum values.

4.4.2.3. Emissions From Toxic Organics

There were 17 organics (15 NMVOCs and 2 NVOCs) in the hydraulic fracturing fluids that were reported as either known human carcinogens or reasonably anticipated to be a human carcinogen (RAHC), which were listed in the U.S. Department of Health and Human Services National Toxicology Program's 13th Report on Carcinogens (Table 4-2) (NTP, 2014). These chemicals included benzene, oxirane and formaldehyde. Of these 17 compounds, the highest median emission was 0.087 kg d^{-1} per well and belonged to benzene, which was only reported to be in 10 wells. The three organics that were exhibited in the hydraulic fracturing fluids of more than 1,000 wells were naphthalene, formaldehyde, and 2-propenamide, which were reported in 11,454 wells, 4,323 wells, and 2,644 wells, respectively. The median emissions were 2.80×10^{-6} kg d^{-1} per well for naphthalene, 2.35×10^{-2} kg d^{-1} per well for formaldehyde, and 3.35×10^{-6} kg d^{-1} per well for 2-propenamide. Previous work by Rogers et al. (2015) also reported naphthalene and 2-butoxyethanol (CASRN: 111-76-2) to be found in more than 20% of the FracFocus reports. Epichlorohydrin (ECH, CASRN: 106-89-8), which can be rapidly adsorbed through skin, gastrointestinal, or lungs (Giri, 1997), was reported in 101 wells with a median emission of 2.27×10^{-4} kg d^{-1} per well. Acetaldehyde (CASRN: 75-07-0), reported in 626 wells with a median emission of 1.24×10^{-2} kg d^{-1} per well, was added as corrosion inhibitor (Stringfellow et al., 2014). Thiourea (CASRN: 62-56-6), also added as corrosion inhibitor (Stringfellow et al., 2014), and was found in 57 wells with a median emission of 8.89×10^{-7} kg d^{-1} per well. The emissions estimated for formaldehyde was 1.35×10^{5} kg, which accounted 16.62% of NMVOCs emission. Formaldehyde with a low boiling point of -19.2 ℃ can quickly evaporate into the atmosphere.

There were 73 organics found to be on the 2011 ATSDR list that were added into the hydraulic fracturing fluids. These chemicals are listed in Table 4-3 and Table A-29 in the Appendix C, and include 60 NMVOCs and 13 NVOCs. A number of these organics also appeared in Table 4-2 due to their potential carcinogenic nature. There were 15 organic compounds (14 NMVOCs and 1 NVOCs) that were found on the Priority List of Hazardous Substances including benzene, dimethylbenzene, methylbenzene, naphthalene, 1,1'-oxybis 2-chloro-ethane (CASRN: 111-44-4), and dichloromethane (CASRN: 75-09-2).

The three organics with the highest toxicity points were 1,1'-oxybis 2-chloro-ethane, benzene, and thiourea. Dimethylbenzene was added in 1,440 wells with a median emission of 3.67×10^{-5} kg d^{-1} per well, and methylbenzene was found in 460 wells with a median emission of 1.41×10^{-4} kg d^{-1} per well. 1,1'-oxybis 2-chloro-ethane was used in 7 wells and dichloromethane occurred in 6 wells. Their median emissions were 1.81×10^{-3} kg d^{-1} per well and 1.17×10^{-3} kg d^{-1} per well, respectively. Methanol (CASRN: 67-56-1), 2-propanol (CASRN: 67-63-0), ethanol (CASRN: 64-17-5), 2-propanone (CASRN: 67-64-1), and acetic acid (CASRN: 64-19-7) were found in 52,744, 35,295, 20,660, 694, and 20,014 wells with the total emissions of 4.50×10^{5} kg, 9.51×10^{4} kg, 6.74×10^{4} kg, 1.13×10^{4} kg, and 1.07×10^{4} kg. Their total emissions accounted 55.50%, 11.74%, 8.31%, 1.40%, and 1.32% of the NMVOCs emissions, respectively.

4.4.2.4. Sensitivity and Uncertainty Analysis

The sensitivity of each input parameter for each organic compound is shown in Figure A-18. Using the median values for the index abs($\log_{10}$(p75:p25)), the most sensitive input parameters were determined to be V_{ca}, followed by T_{AX} and T_{AN}. The highest median value for the abs($\log_{10}$(p75:p25)) index was 0.949, which belonged to V_{ca} and was due to the proportional relationship between the daily loss ($L_{j,W}$, $L_{j,S}$) and V_{ca}. The input parameter t_{fd} affected L_W through the turnover factor (K_N). Meanwhile, growth in t_{fd} induces an increase in L_S. Although L_W was much greater than L_S, t_{fd} had a median value of 0.463 for abs($\log_{10}$(p75:p25)). The median values of abs($\log_{10}$(p75:p25)) were 0.550, 0.513, 0.080, and 0.035 for T_{AX}, T_{AN}, I, and a, respectively. These input parameters were used to calculate the vapor space expansion factor (K_E) and T_{LA}, while T_{LA} was further used to calculated P and vapor density (W_v). The median values of abs($\log_{10}$(p75:p25)) for H_L/H_S, H_S, L, and W were 0.045, 8.6×10^{-11}, 0, and 0. This resulted in p75 to p25 ratios of 1.108 for H_L/H_S, 1.000 for H_S, 1.000 for L, and 1.000 for W, thus indicating that the AP-42 model was not sensitive to H_S, L, and W. Changing the dimensions for the chemical storage tanks (H_S, L, and W) did not affect the total vapor space volume in all the tanks when H_L/H_S was kept constant.

Table 4-2. Organics added into hydraulic fracturing fluids considered potential or known carcinogens.

CASRN	Substance Names	Num. of Wells [a]	Median Emissions (kg d^{-1} per well)	Total Emissions (kg)	Notes
NMVOCs					
106-89-8	Oxirane, (chloromethyl)-	101	2.27E-04	5.77E-01	RAHC [b]
107-13-1	2-Propenenitrile	5	3.56E-02	8.61E-01	RAHC
123-91-1	1,4-Dioxane	762	5.26E-04	9.14E+00	RAHC
50-00-0	Formaldehyde	4,323	2.35E-02	1.35E+05	Known [c]
542-75-6	1-Propene, 1,3-dichloro-	6	3.84E-05	8.66E-04	RAHC
62-56-6	Thiourea	57	8.89E-07	7.04E-02	RAHC
71-43-2	Benzene	10	8.71E-02	2.55E+00	Known
75-07-0	Acetaldehyde	626	1.24E-02	1.82E+02	RAHC
75-09-2	Methane, dichloro-	6	1.17E-03	2.93E-02	RAHC
75-21-8	Oxirane	664	1.91E-02	6.81E+02	Known
75-52-5	Methane, nitro-	25	5.25E-03	3.08E+01	RAHC
75-56-9	Oxirane, methyl-	7	2.18E-03	1.63E-01	RAHC
79-06-1	2-Propenamide	2,644	3.35E-06	1.62E+00	RAHC
91-20-3	Naphthalene	11,454	2.80E-06	3.79E+00	RAHC
98-82-8	Benzene, (1-methylethyl)-	167	2.32E-06	2.42E-02	RAHC
NVOCs					
117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	15	4.48E-10	5.33E-08	RAHC
139-13-9	Glycine, N,N-bis(carboxymethyl)-	22	4.75E-12	6.93E-09	RAHC

[a] number of wells reported the organic in hydraulic fracturing fluids with concentration > 0; [b] Reasonably Anticipated to be a Human Carcinogen; [c] Known to be a human carcinogen; Source: National Toxicology Programe., 2014. Report on Carcinogens, Thirteenth Edition. Research Triangle Park, NC: U.S. Department of Health and Human Services. http://ntp.niehs.nih.gov/pubhealth/roc/roc13/.

Table 4-3. Organics added into hydraulic fracturing fluids and also considered as candidate substances for the Priority List of Hazardous Substances (ATSDR, 2013).

CASRN	Substance Names	Num. of Wells [a]	Median emissions (kg d^{-1} per well)	Total emissions (kg)	Ranks [b]	Toxicity Points [c]
NMVOCs						
100-41-4	Benzene, ethyl-	191	1.39E-03	1.20E+01	116	53
100-44-7	Benzene, (chloromethyl)-	3,217	6.18E-06	1.61E+01	495	178
104-76-7	1-Hexanol, 2-ethyl-	4,736	1.83E-05	8.13E+00	476	53
107-15-3	1,2-Ethanediamine	145	7.56E-05	2.06E-02	680	10
107-21-1	1,2-Ethanediol	36,140	7.37E-05	2.39E+02	410	10
108-10-1	2-Pentanone, 4-methyl-	1,368	3.22E-04	1.40E+01	272	10
108-67-8	Benzene, 1,3,5-trimethyl-	432	7.88E-06	4.70E-02	783	0
108-88-3	Benzene, methyl-	460	1.41E-04	3.66E+01	74	53
108-95-2	Phenol	415	4.01E-05	4.92E+00	179	53
111-46-6	Ethanol, 2,2 -oxybis-	4,746	1.30E-07	3.30E-02	318	178
111-76-2	Ethanol, 2-butoxy-	14,776	1.28E-04	2.70E+02	640	10
112-34-5	Ethanol, 2-(2-butoxyethoxy)-	497	1.51E-06	3.88E-01	699	0
112-40-3	Dodecane	652	1.18E-04	5.80E+00	783	0
1120-21-4	Undecane	1,426	1.66E-03	2.57E+01	783	0
119-65-3	Isoquinoline	208	3.06E-06	1.37E-02	585	53
123-91-1	1,4-Dioxane	762	5.26E-04	9.14E+00	210	178
1330-20-7	Benzene, dimethyl-	1,440	3.67E-05	7.80E+01	62	178
141-43-5	Ethanol, 2-amino-	1,612	4.33E-05	3.64E+01	660	10
50-00-0	Formaldehyde	4,323	2.35E-02	1.35E+05	241	178
526-73-8	Benzene, 1,2,3-trimethyl-	328	8.65E-07	2.64E-02	783	0
57-13-6	Urea	945	9.19E-05	3.91E+00	397	178
57-55-6	1,2-Propanediol	4,472	3.95E-05	4.30E+01	547	53
629-50-5	Tridecane	653	3.51E-05	2.21E+00	783	0
629-59-4	Tetradecane	605	1.97E-05	8.97E-01	783	0
64-17-5	Ethanol	20,660	4.10E-02	6.74E+04	407	53
64-19-7	Acetic acid	20,014	1.75E-02	1.07E+04	642	10
65-85-0	Benzoic acid	135	3.97E-05	4.96E-02	321	10
67-56-1	Methanol	52,744	1.59E-01	4.50E+05	432	10
67-63-0	2-Propanol	35,295	2.83E-02	9.51E+04	308	53
67-64-1	2-Propanone	694	5.32E-01	1.13E+04	186	10
68-12-2	Formamide, N,N-dimethyl-	6,721	6.15E-04	4.69E+02	247	178

Table 4-2. Organics added into hydraulic fracturing fluids and also considered as candidate substances for the Priority List of Hazardous Substances (ATSDR, 2013). (Continued)

CASRN	Substance Names	Num. of Wells [a]	Median emissions (kg d^{-1} per well)	Total emissions (kg)	Ranks [b]	Toxicity Points [c]
71-23-8	1-Propanol	2,265	7.87E-03	3.02E+02	315	178
71-36-3	1-Butanol	1,086	1.28E-03	2.25E+01	643	10
75-07-0	Acetaldehyde	626	1.24E-02	1.82E+02	459	53
78-40-0	Phosphoric acid, triethyl ester	2,484	5.00E-06	4.19E-01	680	10
78-83-1	1-Propanol, 2-methyl-	189	1.28E-01	2.67E+02	651	10
79-06-1	2-Propenamide	2,644	3.35E-06	1.62E+00	680	10
8008-20-6	Kerosine (petroleum)	281	1.69E-05	7.13E-02	783	0
8052-41-3	Stoddard solvent	106	1.39E-02	7.15E+00	783	0
91-20-3	Naphthalene	11,454	2.80E-06	3.79E+00	80	178
95-63-6	Benzene, 1,2,4-trimethyl-	7,232	8.30E-05	4.03E+01	783	0
98-82-8	Benzene, (1-methylethyl)-	167	2.32E-06	2.42E-02	419	10
98-86-2	Ethanone, 1-phenyl-	139	4.33E-06	1.06E-02	648	10
NVOCs						
102-71-6	Ethanol, 2,2 ,2 -nitrilotris-	3,657	8.96E-10	4.07E-04	615	53
112-80-1	9-Octadecenoic acid (Z)-	1,192	1.01E-10	3.37E-04	673	10
124-04-9	Hexanedioic acid	409	8.70E-09	2.06E-04	667	10
1762-95-4	Thiocyanic acid, ammonium salt	989	1.34E-10	8.08E-06	680	10

[a] number of wells reported the organic in hydraulic fracturing fluids with concentration > 0; [b] the top 275 ranked chemicals were considered as the Priority List of Hazardous Substances; [c] the maximum point in toxicity was 600.

The uncertainty quantification from the selected 6 input parameters for the tanks dimensions (H_L/H_S, a), meteorology data (I, T_{AX}, T_{AN}), and chemicals (t_{fd}) was performed using Monte Carlo simulations. The lower and upper boundaries of the 95% confidence interval almost overlapped, indicating that the combinatorial uncertainties of the 6 input parameters on annual emissions were insignificant and are displayed in Figure A-19. The lower and upper boundaries of the 95% confidence interval for the total annual emissions increased from 0.224 kg yr^{-1} in 2008 to 239,927 kg yr^{-1} in 2012, and from 223,985 kg yr^{-1} in 2013 to 252,102 kg yr^{-1} in 2014.

4.4.3. Model Validations

Figure 4-7 compares the emissions from the open flowback pits by the AP-42 Chapter 4.3 (U.S. EPA, 1998) and the stagnant two-film model (Equation A-13 in the Appendix C) in Bloomdahl et al. (2014). Bloomdahl et al. (2014) calculated the emissions of 12 VOCs from the open flowback pits for the hydraulic fracturing wells located in the Marcellus Shale by multiplying the assumed surface area (1451.61 m^2) of the open flowback pits with assumed dimensions of 125 ft × 125 ft with the fluxes calculated by the stagnant two-film model. Our study used AP-42 Chapter 4.3 to calculate the VOCs emissions from the open flowback pits using the same conditions as described in Bloomdahl et al. (2014). The estimated emissions from these two models have a linear relationship with a slope of 1.14 and an adjusted R^2 of 0.999, which is shown in Figure 4-7. The ratio of emissions estimated using the AP-42 Chapter 4.3 to those established using the stagnant two-film model ranged from 0.98 and 1.22, with a median value of 1.11. The emissions from those two models are comparable under the considered situations, and emissions from the AP-42 Chapter 4.3 is be expected to be around 11% higher than those from the stagnant two-film model. The stagnant two-film model considers only the diffusive mechanism, and the AP-42 Chapter 4.3 takes both diffusive and convective mechanisms into consideration. Diffusion and convection are two known mass transfer mechanisms (Hobler and Danckwerts, 2013), which are accounted for using the AP-42 Chapter 4.3 equation. Diffusion takes places when the concentration of the organic compounds reaches an equilibrium between aqueous and gas phases (U.S. EPA, 1998). Convective affects attribute to enhanced volatilization in the gas phase due to the air movement along the surface of water (U.S. EPA, 1998; Hobler and

Danckwerts, 2013). Taking these two influences into account, explains why the emissions from the AP-42 Chapter 4.3 were around 11% higher than those from the stagnant two-film model under the same conditions.

Figure 4-8 displays the aqueous concentrations and emissions of four organic compounds (xylenes, toluene, benzene, and ethylbenzene), which were found both in this study and Bloomdahl et al. (2014). Figure 4-8.a shows their aqueous concentrations in the open flowback pits, chemical additives, and hydraulic fracturing fluids. The mean concentrations for xylenes, toluene, benzene, and ethylbenzene were 0.390, 0.240, 0.124, and 0.049 ppm, respectively, in the flowback pits. The mean concentrations in the chemical additives were 2.9×10^4 ppm for xylenes, 2.2×10^3 ppm for toluene, 5.2×10^3 ppm for benzene, and 6.1×10^4 ppm for ethylbenzene. The mean aqueous phase concentrations in the hydraulic fracturing fluids were 872, 49, 82, and 1.5×10^3 ppm for xylenes, toluene, benzene, and ethylbenzene, respectively. Concentrations for the four organics in the open flowback pits were lower than those in hydraulic fracturing fluids due to the chemical reactions under the high pressures and dilution by the water in the formation after being injected into the well (Vidic et al., 2013).

Figure 4-8.b presents the emissions for the total xylenes, toluene, benzene and ethylbenzene from the open flowback pits by the stagnant two-film model in Bloomdahl et al. (2014), from the open flowback pits by the AP-42 Chapter 4.3 under the same situations described in Bloomdahl et al. (2014), and from chemical storage tanks by the AP-42 Chapter 7. The mean emissions per well for the total xylenes, toluene, benzene, and ethylbenzene were 0.147, 0.104, 0.058, and 0.018 kg d^{-1}, respectively, from the open flowback pits by the stagnant two-film model. The mean emissions per well from the open flowback pits calculated using the AP-42, Chapter 4.3 was 0.166 kg d^{-1} for the total xylenes, 0.110 kg d^{-1} for toluene, 0.061 kg d^{-1} for benzene, and 0.021 kg d^{-1} for ethylbenzene., The mean emissions per well for the total xylenes, toluene, benzene, and ethylbenzene were 0.013, 0.024, 0.113, and 0.014 kg d^{-1}, respectively, and were calculated from the AP-42 Chapter 7 equation for the storage tanks.

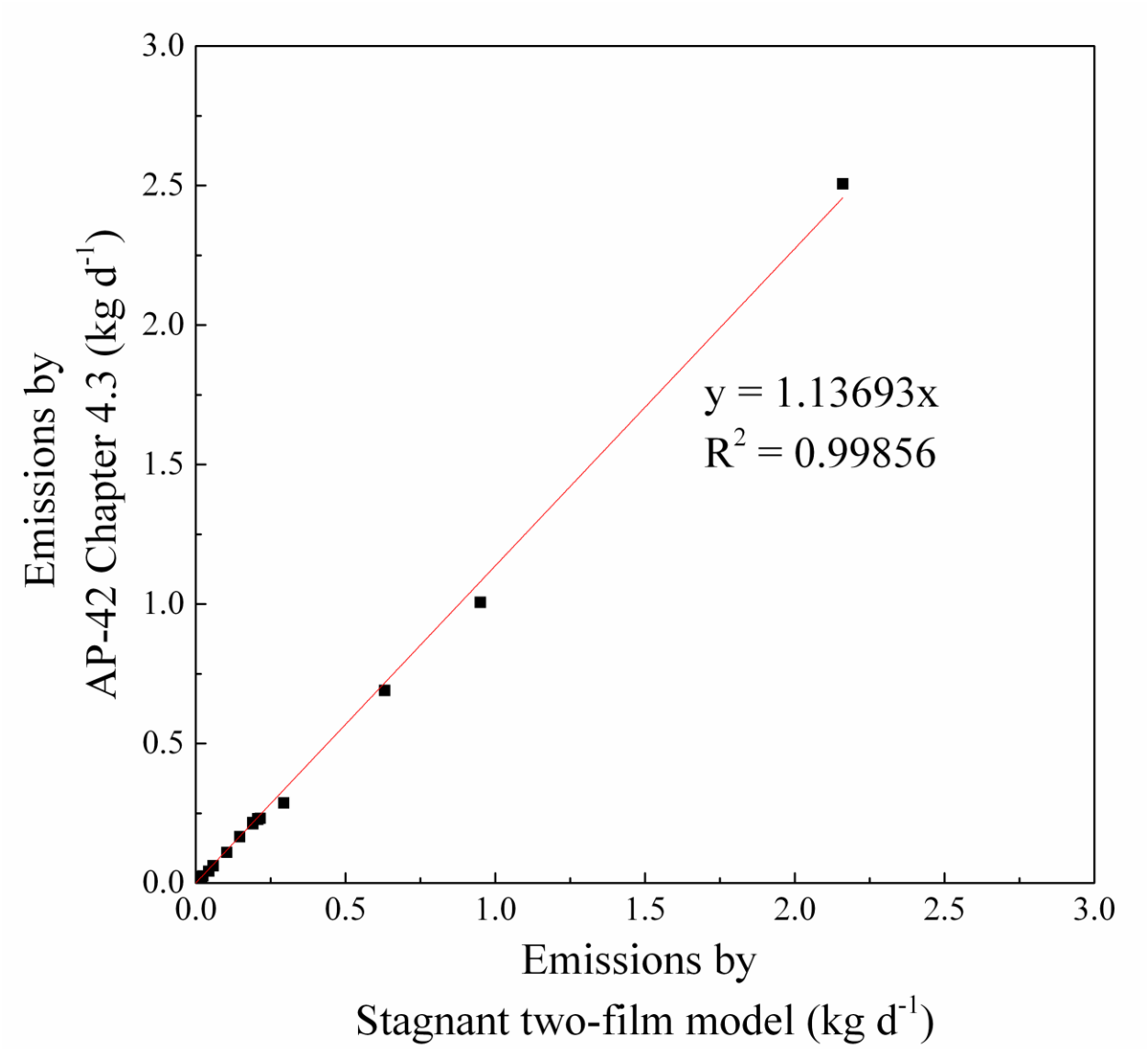

Figure 4-7. Emission rates (kg d^{-1}) from the open flowback pits by the AP-42 Chapter 4.3 (U.S. EPA, 1998) and the stagnant two-film model (Bloomdahl et al., 2014).

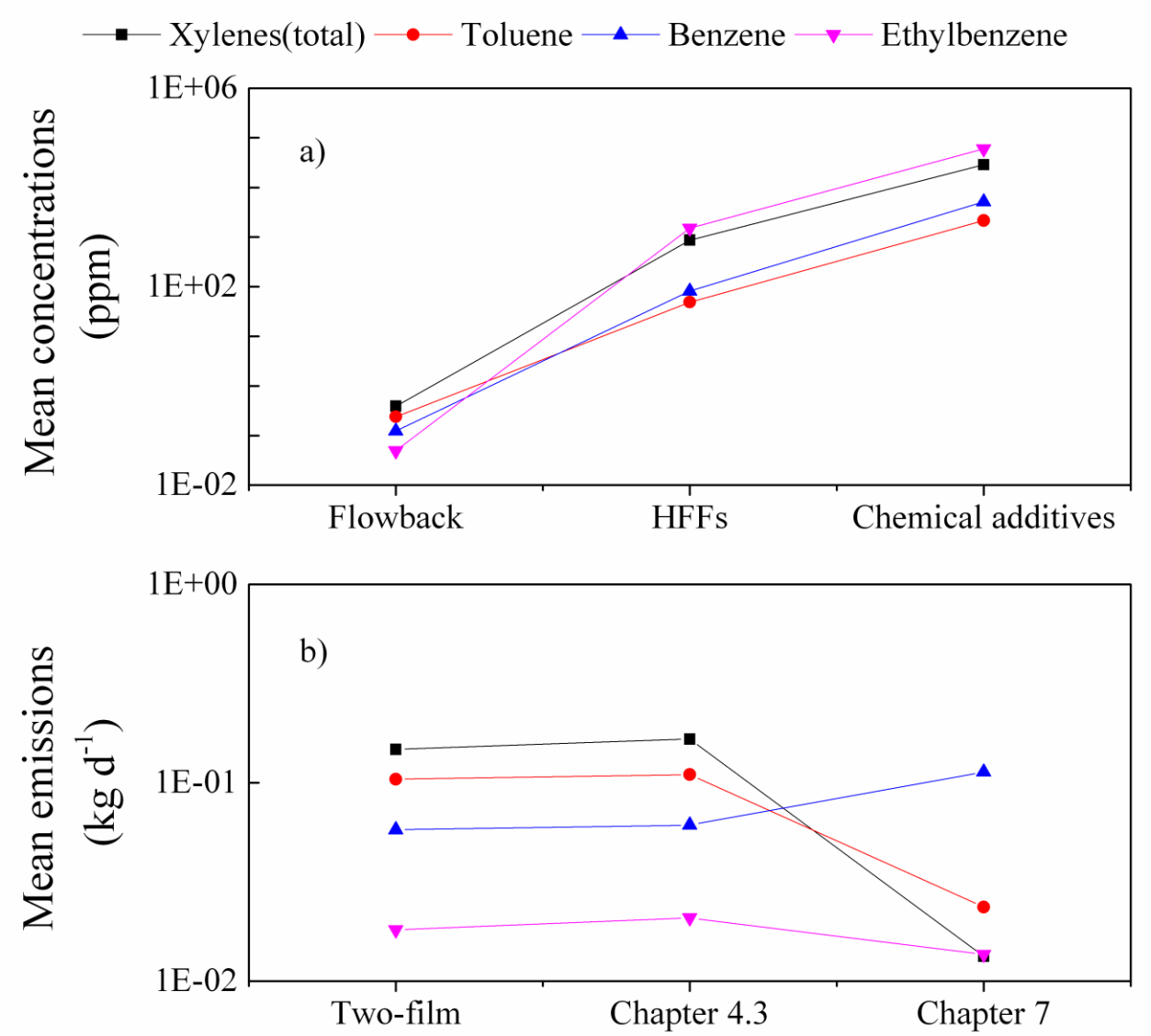

Figure 4-8. Estimated mean aqueous concentrations and mean emissions of the total xylenes, toluene, benzene, and ethylbenzene using AP-42 Chapters 4.3 and 7 and Bloomdahl et al. (2014): a) mean aqueous concentrations in the open flowback pits in Bloomdahl et al. (2014), chemical additives, and hydraulic fracturing fluids; and b) mean emissions from the open flowback pits estimated using stagnant two-film model in Bloomdahl et al. (2014), from the open flowback pits by the AP-42 Chapter 4.3, and from chemical storage tanks by the AP-42 Chapter 7.

The emissions from the open flowback pits were comparable to the stagnant two-film model and the AP-42 Chapter 4.3. The emissions from the open flowback pits by the stagnant two-film model and from chemical storage tanks estimated using the AP-42 Chapter 7 model were differed by six order of magnitude in the chemical additives. The mean emissions per well for xylenes and toluene estimated for the chemical storage tanks were lower due to the fact that the flowback pits are open to the atmosphere making it more favorable for organic evaporation to take place. Henry's law constants were used in the stagnant two-film model to calculate emissions from the open flowback pits. Since the chemical additives in the storage tanks are not dilute aqueous solutions, Raoult's law was suggested by U.S. EPA (2006) to replace Henry's law in the AP-42 Chapter 7. As shown in Table A-30 in the Appendix C, the vapor pressure of benzene was much higher compared to the other three organic compounds while all of them have comparable Henry's law constants, explaining why the mean benzene emissions per well from the chemical storage tanks was greater than that from the open flowback pits.

4.5. Conclusions

The emissions from the organic chemical additives in 72,023 hydraulic fracturing wells were estimated using the AP-42 model for vertical fixed-roof liquid storage tanks in this study. The median emission was 0.221 kg d^{-1} per well. The total annual emissions increased from 0.221 kg yr^{-1} in 2008 to 250,665 kg yr^{-1} in 2012 and remained steady constant in 2013 and 2014. The main contributor to the annual total emissions was NMVOCs. The median well emission was 0.110 kg per well in 2008 and 0.786 kg per well in 2014, which shows an increasing trend. The increase in well emissions was induced by the growth tendencies in volumes of chemical additives in each well, instead of emissions per cubic meter chemical additives.

The 50th percentiles for median emissions of each organic were 3.48×10^{-9} kg d^{-1} for each well. The ratios of the highest to lowest values in the 50th percentiles for median organic emissions in each well kg d^{-1} per well and total organic emissions in kg were 128.92 and 97.77. This indicates the organic emissions varied greatly among each state. According to the correlation analysis, the 50th percentiles for median organic emissions (kg d^{-1} per well) and total emission (kg) were positively related with the percentage of NMVOCs, and negatively correlated with the percentage of NVOCs. The 50th percentile for median

emissions of each organic compound was much greater for NMVOCs due to their high volatilities. Furthermore, 60 NMVOCs belonged to the 2011 ATSDR list of 847 candidate substances. Of the total emissions caused by all NMVOCs, 95.14% were due to the substances on the ATSDR candidate substances list.

CHAPTER 5

POTENTIAL OCCUPATIONAL INHALATION EXPOSURES OF TOXIC ORGANICS FROM CHEMICAL STORAGE TANKS IN HYDRAULIC FRACTURING USING THE AERMOD MODELING

A version of this chapter are prepared for a publication:

Chen, H. and K. E. Carter (2016). " Potential Occupational Inhalation Exposures of Toxic Organics from Chemical Storage Tanks in Hydraulic Fracturing Using the AERMOD Modeling: A Modeling Approach " (submitted to *Environment Pollution*)

Highlights

- Occupational inhalation risks estimated using 60,644 hydraulic fracturing wells
- Methanol posed an acute exposure for non-cancer risk in 7,282 wells
- Formaldehyde had an acute and chronic exposure for cancer risk for 4,267 and 3,470 wells, respectively.

5.1. Abstract

Natural gas exploitation in the United States (U.S.) increased rapidly from 2008 to 2014 due to the advances in hydraulic fracturing and horizontal drilling technologies. However, various toxic chemicals used in hydraulic fracturing fluids may influence the inherent health risks associated with hydraulic fracturing. This study investigated the occupational inhalation exposures and associated risks of the evaporated organic compounds from chemical storage tanks and flowback pits used in hydraulic fracturing in the U.S. Potential risks were evaluated based on radial distances between 5 m and 180 m from the wells for 23 organics with known inhalation reference concentration (RfC) or inhalation unit risks (IUR). Results show that out of 60,644 well, chemicals used in 12.4% of the wells that posed a potential acute exposure for non-cancer risks and 0.11% of the well with that may cause chronic exposure for non-cancer risks. Chemicals used in 7.5% and 5.8% of the wells were associated with an acute exposure that can potentially cause cancer and a chronic exposure that can potentially cause cancer, respectively. There were eight organic compounds that may cause the acute exposure for non-cancer risks (>1) in 7,460 wells. Methanol posed an acute exposure for non-cancer risks between 1.00 and 45.49 in 7,282 wells indicating that methanol was the major compound from the chemical storage tanks associated with the acute exposure for non-cancer risks in the hydraulic fracturing wells. Wells with chemicals containing formaldehyde showed

that the acute and chronic exposures for cancer risks were greater than 10^{-6}, indicating formaldehyde was the dominant contributor to both the potential acute and chronic exposures for cancer risks in hydraulic fracturing wells. Due to the other existing on-site emission sources of volatile organic compounds (VOCs) and the geographically overlapped air concentrations from other surrounding wells, chemical emissions from storage tanks and flowback pits used in this study were lower than the field concentrations, and higher occupational inhalation risks may be expected.

5.2. Introduction

5.2.1. Background

Hydraulic fracturing is a stimulation technology for recovering natural gas from shale or rock formations. The process is performed by injecting large volumes of hydraulic fracturing fluids into the well at high pressure (Chen and Carter, 2016). Hydraulic fracturing fluids are made up of approximately 0.5 – 2 % chemical additives and the remaining water and proppants (Arthur et al., 2009; Gregory et al., 2011). Chemical additives employed in hydraulic fracturing fluids are used for reducing friction, inhibiting corrosion and the formation of scale, and as biocides (Arthur et al., 2009; Gregory et al., 2011; Aminto and Olson, 2012). Advances in hydraulic fracturing and horizontal drilling technologies have enabled the increased the oil and natural gas recovery from tunconventional reservoirs in the United States (U.S.) (Akyon et al., 2015). However, the adverse environmental and health effects associated with hydraulic fracturing have become a concern.

Hydraulic fracturing fluids pose the adverse health risks primarily due to the addition of the toxic chemicals (Wattenberg et al., 2015). Of all the chemicals used, it was discovered that there were 13 different carcinogens contained in 95 products used by the hydraulic fracturing operators (U.S. House of Representatives, 2011). Stringfellow et al. (2014) identified 81 common chemicals in hydraulic fracturing fluids, and found 5 confirmed or suspected carcinogens (ethanol, naphthalene, diethanolamine, acetaldehyde, and thiourea). After reviewing the inhalation toxicity of these compounds in the literature, it was suggested that the inhalation exposure cannot be overlooked and should be further investigated. Until

now, no report regarding the potential inhalation risks brought on by the chemical additives before being added into hydraulic fracturing fluids existed. Storing and emptying of the storage tanks for chemical additives used in hydraulic fracturing fluids may cause the evaporation of volatile organic compounds (VOCs) into the atmosphere contributing to the effects on human health, especially that of the workers around the wells.

Atmospheric dispersion models are used to simulate the distribution of air pollutants and are able to predict their concentrations, which is expensive and time-consuming to perform using field and lab measurements (Langner and Klemm, 2011). AERMOD, developed by the American Meteorological Society (AMS) and U.S. Environmental Protection Agency (U.S. EPA), may be used to model the dispersion of air pollutants from a variety of stationary industrial sources (*i.e.* point, area, and volume sources) over short-range (<50 km) (Igri et al., 2011; Gibson et al., 2013; Rood, 2014). Input data for AERMOD include: 1) emission sources, 2) meteorological data, and 3) receptor locations (U.S. EPA, 2004b), but does not take into account the chemical reactivity of the pollutants as these are considered insignificant within the 50 km × 50 km domain being studied (Gibson et al., 2013).

In order to evaluate the adverse effects of the toxic organic chemical vapors on the workers in hydraulic fracturing, this study coupled AERMOD with inhalation risk assessment (U.S. EPA, 2009). Since the open flowback pits in hydraulic fracturing wells were reported to be another potential emission source for occupational inhalation risks (Bloomdahl et al., 2014), the combined occupational inhalation risks caused by the open flowback pits and the chemical storage tanks were investigated. The objectives of this study were: 1) to investigate the toxic organic air concentrations due to emissions from chemical storage tanks; 2) to estimate the occupational non-carcinogenic and carcinogenic risks by toxic vapors from chemical storage tanks through the acute and chronic inhalation exposures; and 3) to investigate the combined inhalation risks from the chemical storage tanks and the open flowback pits.

5.2.2. Motivations and hypothesis

Motivations:

First motivation: investigate the spatial and temporal distributions of organic air concentrations around the hydraulic fracturing wells by using AERMOND dispersion model

Second motivation: estimate the possibility of the non-carcinogenic and carcinogenic exposure risks to workers through the inhalation exposure

Hypotheses:

First hypothesis (H_0): Toxic vapors from chemical storage tanks do not have the potential to cause health consequences.

5.2.3. Summary

Conclusion about the Tested Hypothesis:

The results obtained in this study and related with the tested hypothesis are illustrated in Table 5-1, and the conclusion about the tested hypothesis is shown as follows:

1) The study in this Chapter do not support H_0 in the first hypothesis.

Table 5-1 Results related with the hypotheses

Hypotheses	Results related with the hypothesis
First hypothesis	• A total of 7,527 wells had risk values that showed a potential acute exposure for non-cancer risk. • A total of 4,567 wells had acute exposure for cancer risks from 1.00×10^{-6} to 0.94, and 3,518 wells with the chronic exposure for cancer risks from 1.00×10^{-6} to 6.90×10^{-2}. • The percentage of wells with the possibilities of the acute exposure for non-cancer risks, chronic exposure for non-cancer risks, acute exposure for cancer risks, and chronic exposure for cancer risks on workers were 12.41%, 0.11%, 7.53%, and 5.80%, respectively

Contributions to the Overall Hypothesis and Objective:

The first hypothesis and the second motivation are the overall hypothesis and objective.

Strengths:

1) Three types of air concentrations at each circle with the radii from 5 m to 180 m away from the chemical storage tanks were calculated.

2) The combined exposure risks due to the emissions from chemical storage tanks and open flowback pits were investigated.

Limitations:

1) The meteorological data for AERMOD was obtained from the nearest observation stations, and was not the field data at the location of wells.
2) Due to the lack of CAS number, emissions of only 475 organics out of 2,302 chemicals added in HFFs were identified. Out of 475 organics, 23 organics with the RfC or IUR values from IRIS were selected for inhaled exposure evaluations. This would lead to the underestimated exposure risks due to the fact the exposures for some toxic chemicals without the information of their RfC or IUR values were not estimated.

Future Directions:

1) Our study is about the possibility of exposure risks by chemical storage tanks. There are other emission sources in the hydraulic fracturing wells which would also cause the inhalation exposure.
2) Epidemiological data about the effects of hydraulic fracturing on workers would further valid the conclusions from our study.

5.3. Methodology

5.3.1. AERMOD Descriptions

Daily average air concentrations from each hydraulic fracturing well were simulated by AERMOD. The emission sources from the chemical storage tanks were considered as volume sources, and the input parameters for the emission sources are shown in Table A-31 (in the Appendix D). The well data in this study was obtained from the website www.FracFocus.org (FracFocus, 2015), and was described in detail in Chen and Carter (2016). The organic chemical emissions from the chemical storage tanks and flowback pits for 70,203 wells were estimated using AP-42 Chapters 4.3 and 7 (U.S. EPA, 2006). Hourly meteorological data for each hydraulic fracturing well was obtained through AERMET (U.S. EPA, 2004a) using the surface and upper air data from the nearest observation stations. The surface and upper air data

was obtained from the Integrated Surface Hourly Database (ISHD) and the Earth System Research Laboratory (ESRL) Radiosonde Database, respectively. Both the ISHD and ESRL databases are part of the National Oceanic and Atmosphere Administration (NOAA). The hydraulic fracturing wells were assumed to be located on flat land therefore no terrain data was used in this study.

Distances, wind speed and direction, are closely related to the distribution of the air concentration from and around the emission sources (Venkatram et al., 2013), which further the inhalation exposure and associated risks by dispersing the pollutants (Brown et al., 2015). The location of the chemical storage tanks and the flowback pits were considered to be center of the radii. Because the location of the hydraulic fracturing wells related to the emission sources were not reported, the average, minimum, and maximum concentrations were calculated for each of the following radii: 5, 10, 20, 50, 80, 120, 150 and 180 m, which are distances from the emissions sources to the receptors as shown in Figure A-21 in the Appendix D. Receptors are used to represent the workers on site. There were 36 receptors evenly distributed within each circle with the previously mentioned radii. The receptor height was uniformly set as 1.70 m, which is the average female (1.63 m) and male (1.76 m) height with the age of 30-39 years in the U.S. (Fryar et al., 2012).

5.3.2. Health Risk Assessment

When estimating inhalation risk, U.S.EPA recommended using exposure concentration ($\mu g \cdot m^{-3}$) for replacing contaminant intake ($mg\ kg^{-1}\ day^{-1}$) based on inhalation rate and body weight (U.S. EPA, 2009). Because of the different contact durations, exposures can be divided into acute, sub-chronic, and chronic exposures, where the exposure time is ≤ 24 hr, 24 hr - 10% of the life span, and > 10% of the life span, respectively (U.S. EPA, 2009). The exposure concentration is equal to air contaminant concentration for acute exposures (Equation 5-1). For the sub-chronic and chronic exposure, exposure time, exposure frequency, duration and average time were taken into consideration (Equation 5-2) (U.S. EPA, 2009). The non-cancer and cancer exposure risk through the inhalation exposures were estimated using Equation 5-3 and Equation 5-4, respectively.

Equation 5-1

$$\mathrm{EC} = \mathrm{CA}$$

Equation 5-2

$$\mathrm{EC} = \frac{CA \times ET \times EF \times ED}{AT}$$

Equation 5-3

$$\mathrm{HQ} = \frac{EC}{RfC \times 1000\ \mu\mathrm{g/mg}}$$

Equation 5-4

$$\mathrm{Risk} = \mathrm{IUR} \times \mathrm{EC}$$

where EC is the exposure concentration (μg m^{-3}); CA is the air contaminant concentration (μg m^{-3}); ET is the exposure time (8 hr d^{-1}); EF is the exposure frequency (250 d yr^{-1}) (U.S. EPA, 1991); ED is the exposure duration (25 yr) (U.S. EPA, 1991); AT is the average time, which was calculated as 78 yr × 365 d yr^{-1} × 24 hr d^{-1} = 683,280 hr (U.S. EPA., 2011); HQ is the hazard quotient (unitless); RfC is the inhalation reference concentration (mg m^{-3}); Risk is the cancer exposure risk (unitless); IUR is the inhalation unit risk ($(\mu g\ m^{-3})^{-1}$).

The parameters for the chronic exposure durations in Equation 5-2 (ET, EF, ED, and AT) are summarized in Table A-33 (in the Appendix D). The RfC and IUR values for 23 organic compounds were obtained from U.S. EPA's Integrated Risk Information System (IRIS) (Table A-34 in the Appendix D). There were 21 organics with RfC values and 10 organics with IUR values. The risks associated with the organic compounds used in a hydraulic fracturing well were combined and considered to be the risk for the well (shown in Equation A-36 and Equation A-37 in the Appendix D). While HQ ≤ 1 presents the exposure level is less than the reference dose and indicates negligible health risks, HQ > 1 suggests the potential adverse health effects (U.S. EPA, 1989; Lau et al., 2014; Saleem et al., 2014) and HQ > 10 suggests a high non-cancer exposure risk (Zhou et al., 2014a). U.S. EPA (1997) suggested the cancer risk range of 10^{-6} to 10^{-4} as the acceptable levels. The cancer risks lower than 10^{-6} indicates that there is one out of 1,000,000 persons with the chance of developing the cancer and are considered to be negligible in this study (Niu et

al., 2014; Ollson et al., 2014; Saleem et al., 2014), and the cancer risks greater than 10^{-4} are considered to be an unacceptable risk (Wang et al., 2013; Saleem et al., 2014).

5.4. Results and Discussion

5.4.1. Air Concentrations

Table A-35 (in the Appendix D) shows the radial distance of the minimum, mean and maximum air concentrations from the emissions source for each well The radius of 5 m had the largest percentage (60.3%) of wells, followed by 28.7% at the radius of 10 m and 7.3% at the radius of 20 m. Table 5-2 shows the median air concentrations for 23 organic compounds estimated by AERMON at the radius of 5 m. Comparing the values listed in Table 1 to the recommended exposure limits (RELs) suggested by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) showed that the median values in the minimum, average, and maximum air concentrations at the distance of 5 m were small for all of the listed organics. For example, the median value for the maximum air concentrations of 2-butoxyethanol (CASRN: 111-76-2) was 1.98×10^{-6} mg m^{-3}, which is eight magnitudes lower than REL of 240 mg m^{-3} recommended by OSHA. This suggests that the air concentrations for the over half of the wells located within the 5 m radius met the requirements on the RELs by NIOSH and OSHA.

Comparisons of the air concentrations estimated in this study and measured in the previous studies by McKenzie et al. (2012) and Colborn et al. (2014) are listed in Table A-36 (in the Appendix D). McKenzie et al. (2012) collected air samples from natural gas development and well completion areas in Garfield County, Colorado. Colborn et al. (2014) gathered air samples in Garfield County, Colorado from July, 2010 to October, 2011. There were 130 natural gas wells and 2 vertical drilling well pads within 1 mile from the sampling site. The measured air concentrations in these two studies were higher than the average air concentrations, at a distance of 180 m, estimated using emissions from chemical storage tanks (shown in Table A-36 in the Appendix D). The higher air concentration may be attributed to the variations exhibited as the distance from the emission sources increases. Although the positions of each well within the sample site were not reported, the air concentrations in established in McKenzie et al. (2012) and Colborn et al.

(2014) were overlapped air concentrations from all the wells located around the sample site. Further, concentrations in the air samples may be enhanced when the sampling sites were directly located downwind of the hydraulic fracturing wells. Apart from the influences of the overlapped air concentrations and wind directions, other emission sources for toxic organic compounds (Bloomdahl et al., 2014; Werner et al., 2015) may also lead to the higher air concentrations in the samples from the McKenzie et al. (2012) and Colborn et al. (2014) studies compared with the air concentrations in this study estimated using emissions data for the chemical storage tanks.

5.4.2. Associated Inhalation Exposures

5.4.2.1. Wells

Table 5-3 shows the inhalation risks associated with the emissions from chemical storage tanks used for hydraulic fracturing wells based on the average and maximum air concentrations at the radius of 5 m away from chemical storage tanks. There were 60,644 wells where the 23 organic compounds were used in the additives that made up the hydraulic fracturing fluids (listed in Table A-34 in the Appendix D). The 50th percentile of the non-cancer and cancer exposure risks based on average air concentrations for all the wells were less than 1 and 10^{-6}, respectively, which shows there were negligible risks for more than half of the wells. However, when considering the maximum air concentrations located 5 m away from the emission source, the 99th percentile of the acute and chronic exposures for non-cancer risk and the acute and chronic exposures for cancer risk for all the wells were 2.28, 0.17, 3.06×10^{-3}, and 2.24×10^{-4}, respectively, indicating that a potential acute exposure for non-cancer risk, the acute exposure for cancer risk, and the chronic exposure for cancer risk would occur in at least 1% of the wells. For the acute exposure for non-cancer risks based on the maximum air concentrations, the 99th percentile was greater than 1 for all the well except those located in Colorado and Louisiana. The 99th percentile for the chronic exposure for non-cancer risk based on the maximum air concentrations was less than 1 for the wells in all the states. Based on the maximum air concentrations within the 5 m radius more than 1% of the wells in each state may be associated with acute and chronic exposures for cancer risks.

Table 5-2. Air concentrations estimated by AERMOS using a radius of 5 m are listed.

Substance Name	CASRN	Num. of Wells	Air Concentrations (mg m^{-3})			NIOSH RELs (mg m^{-3}) [d]		OSHA RELs(mg m^{-3}) [d]	
			50th in Min. [a]	50th in Aver. [b]	50th in Max. [c]	TWA	ST	TWA	ST
Acetaldehyde	75-07-0	626	0.00E+00	0.00E+00	0.00E+00	NA	NA	360	NA
Acrylamide	79-06-1	2,644	0.00E+00	0.00E+00	0.00E+00	0.03 [skin]	NA	0.3 [skin]	NA
Acrylic acid	79-10-7	82	1.17E-04	8.63E-04	3.17E-03	6	NA	NA	NA
Acrylonitrile	107-13-1	5	1.69E-04	1.78E-03	8.37E-03	21.7 [skin]	NA	21.7 [skin]	NA
Aniline	62-53-3	25	0.00E+00	0.00E+00	0.00E+00	NA	NA	19 [skin]	NA
Benzene	71-43-2	10	5.06E-04	4.12E-03	1.66E-02	0.319	3.19	3.19	13.95
Bis(chloroethyl)ether	111-44-4	7	0.00E+00	0.00E+00	0.00E+00	30	60	90	NA
Cumene	98-82-8	167	1.53E-08	1.15E-07	4.59E-07	245 [skin]	NA	245 [skin]	NA
Dichloromethane	75-09-2	6	1.28E-05	1.02E-04	4.13E-04	NA	NA	86.75	433.75
1,3-Dichloropropene	542-75-6	6	4.33E-07	3.46E-06	1.41E-05	5 [skin]	NA	NA	NA
N,N-Dimethylformamide	68-12-2	6,721	0.00E+00	0.00E+00	0.00E+00	30 [skin]	NA	30 [skin]	NA
1,4-Dioxane	123-91-1	762	0.00E+00	0.00E+00	0.00E+00	NA	NA	360 [skin]	NA
Epichlorohydrin	106-89-8	101	1.93E-07	1.45E-06	5.70E-06	NA	NA	19 [skin]	NA
Ethylbenzene	100-41-4	191	6.76E-06	4.80E-05	2.84E-04	435	545	435	NA
2-Butoxyethanol	111-76-2	14,776	6.57E-08	4.82E-07	1.98E-06	24 [skin]	NA	240 [skin]	NA
Formaldehyde	50-00-0	4,323	3.35E-05	2.53E-04	9.44E-04	0.01968	NA	0.9225	2.46
Methanol	67-56-1	52,744	8.87E-05	6.74E-04	2.90E-03	260	325	260	NA
Methyl isobutyl ketone	108-10-1	1,368	2.73E-07	2.17E-06	1.14E-05	205	300	410	NA
Naphthalene	91-20-3	11,454	1.15E-10	8.31E-10	3.12E-09	50	75	50	NA
Propylene glycol monomethyl ether	107-98-2	14	1.62E-05	1.33E-04	6.68E-04	360	540	NA	NA
Propylene oxide	75-56-9	7	1.41E-05	1.03E-04	4.63E-04	NA	NA	240	NA
Toluene	108-88-3	460	1.18E-06	9.24E-06	4.06E-05	375	560	754	NA
Xylenes	1330-20-7	1,440	4.34E-08	3.19E-07	1.27E-06	NA	NA	NA	NA

[a] 50th percentile in minimum air concentrations;
[b] 50th percentile in average air concentrations;
[c] 50th percentile in maximum air concentrations;
[d] sources: NIOSH Pocket Guide to Chemical Hazards, http://www.cdc.gov/niosh/npg/, Accessed on 4/11/2016.
NIOSH: The National Institute for Occupational Safety and Health.
OSHA: Occupational Safety and Health Administration.
RELs: Recommended Exposure Limits.
TWA: time-weighted average concentration.
ST: short-term exposure limit.

Table 5-4 summarizes the wells with the non-cancer and cancer exposure risks based on the maximum air concentration for all the receptors located between the 5 to 180 m from the emission sources. A total of 7,527 wells had risk values that showed a potential acute exposure for non-cancer risk existed. The well with the highest acute exposure for non-cancer risk of 45.49 was located in Oklahoma. For the acute exposure for non-cancer risks, the number of wells were 6,949, 431, and 147 with $1 \leq$ risks < 5, $5 \leq$ risks < 10, and $10 \leq$ risks, respectively. This indicates that most of the wells had an acute exposure for non-cancer risk between 1 and 5. There were 65 wells with potential chronic exposure for non-cancer risks ranging from 1.00 and 3.33. Among the 65 wells, 41 wells were located in Texas while the others were located in Arkansas, Louisiana, North Dakota, Oklahoma, and Pennsylvania. A total of 4,567 wells had acute exposure for cancer risks from 1.00×10^{-6} to 0.94, and 3,518 wells with the chronic exposure for cancer risks from 1.00×10^{-6} to 6.90×10^{-2}. Among these wells, there were 2,892 and 3,126 wells with the acute and chronic exposures for cancer risks between 10^{-6} and 10^{-4}, respectively.

Previous studies show there were no health risks caused by hydraulic fracturing for communities. Zielinska et al. (2014) suggested that the air quality within a distance greater than 100 m downwind of the emissions source would not be affected by gas wells and compressor stations. Shale gas exploitation in the Barnett Shale region has not led to the adverse health in community-wide inhalation exposures (Bunch et al., 2014). Bloomdahl et al. (2014) indicated no adverse chronic non-cancer and cancer exposure risks were posed by 12 of the VOCs emitted from the open flowback pits used in the hydraulic fracturing operations located in Marcellus Shale. However, their assumed cancer exposure frequency and duration were much shorter compared with those values adopted in previous studies (shown in Table A-33 in the Appendix D), which would lead to the underestimated risks shown in their study. Based on the 95% upper confidence interval (UCL) of the average air concentrations, McKenzie et al. (2012) presented the chronic exposure for non-cancer risks were 0.4 for the distance > 0.5 mile and 1 for the distance ≤ 0.5 mile, and the cancer exposure risks were 6×10^{-6} for the distance > 0.5 mile and 10^{-5} for the distance ≤ 0.5 mile. Paulik et al. (2015) indicated that the air concentrations of polycyclic aromatic hydrocarbons (PAHs) at the sampling sites with the distances of 0.04-3.2 miles to an active natural gas well pad increased by one order of

magnitude in rural areas after natural gas activity had taken place, which posed an adverse health effect on both the workers and the residents. Their study showed that the chronic exposure for cancer risks associated with the measured PAHs in the sites closest to the emissions sources were 2.9×10^{-4} for the residents and 5.9×10^{-5} for the workers.

5.4.2.2. Organics

Table 5-5 presents the inhalation exposure for non-cancer risks for 21 organics and the inhalation exposure for cancer risks for 10 organics based on the average and maximum air concentrations at a radius of 5 m away from chemical storage tanks. The 50th percentile risks were calculated based on the average air concentrations, while the 99th percentile risks were attained using the maximum air concentrations. For the non-cancer risks, the 50th percentile for the acute and chronic exposures were lower 1 for all the 21 organics, and the 99th percentiles for the acute and chronic exposures were higher than 1 for some organics. Acetaldehyde, acrylic acid, acrylonitrile, benzene, epichlorohydrin, and methanol posed risks of 2.52, 22.43, 8.11, 1.86, 14.19, and 2.31, respectively, for the acute exposure, which were within the 99th percentile. The 99th percentile for acrylic acid was 1.64 and epichlorohydrin was 1.04 for the chronic exposures. For the cancer risks the 50th percentile for acute exposure were 1.21×10^{-4} for acrylonitrile, 3.21×10^{-5} for benzene, and 3.29×10^{-6} for formaldehyde. Acrylamide, acrylonitrile, benzene, bis(chloroethyl)ether (CASRN: 111-44-4), dioxane (CASRN: 123-91-1), epichlorohydrin, formaldehyde, and propylene oxide (CASRN: 75-56-9) had an acute exposure for cancer risks of 1.00×10^{-6}, 1.10×10^{-3}, 4.36×10^{-4}, 1.25×10^{-4}, 5.78×10^{-6}, 1.70×10^{-5}, 4.77×10^{-3}, and 3.16×10^{-6}, respectively, in the 99th percentile. Only acrylonitrile and benzene posed a chronic exposure for cancer risks in the 50th percentile of 8.83×10^{-6} and 2.35×10^{-6}. Acrylonitrile, benzene, bis(chloroethyl)ether, epichlorohydrin, and formaldehyde had a chronic exposure for cancer risks of 8.07×10^{-5}, 3.19×10^{-5}, 9.17×10^{-6}, 1.25×10^{-6}, and 3.49×10^{-4}, respectively, in the 99th percentile.

Table 5-3. Potential inhalation risks caused by emissions from chemical storage tanks used for hydraulic fracturing are listed. Risks were estimated by using a radius of 5 m.

States	Num. of wells	Non-cancer				Cancer			
		Acute		Chronic		Acute		Chronic	
		50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]
All the states	60,664	7.71E-04	2.28E+00	5.65E-05	1.67E-01	0.00E+00	3.06E-03	0.00E+00	2.24E-04
Arkansas (AR)	2,424	3.64E-02	8.50E+00	2.67E-03	6.22E-01	5.50E-09	1.10E-04	4.02E-10	8.03E-06
California (CA)	429	5.43E-02	2.12E+00	3.97E-03	1.55E-01	5.98E-06	8.43E-05	4.38E-07	6.17E-06
Colorado (CO)	5,734	6.60E-04	9.13E-01	4.83E-05	6.68E-02	1.60E-06	2.39E-04	1.17E-07	1.75E-05
Kansas (KS)	410	4.65E-03	1.56E+00	3.40E-04	1.14E-01	4.23E-09	1.44E-03	3.09E-10	1.05E-04
Louisiana (LA)	953	0.00E+00	9.82E-01	0.00E+00	7.19E-02	1.77E-07	2.06E-02	1.30E-08	1.51E-03
Montana (MT)	336	0.00E+00	1.38E+00	0.00E+00	1.01E-01	0.00E+00	4.13E-04	0.00E+00	3.02E-05
North Dakota (ND)	4,444	0.00E+00	1.68E+00	0.00E+00	1.23E-01	0.00E+00	3.88E-04	0.00E+00	2.84E-05
New Mexico (NM)	2,036	4.40E-03	1.24E+00	3.22E-04	9.05E-02	1.91E-06	2.75E-03	1.39E-07	2.01E-04
Ohio (OH)	606	0.00E+00	1.02E+00	0.00E+00	7.44E-02	0.00E+00	3.90E-04	0.00E+00	2.85E-05
Oklahoma (OK)	5,823	1.23E-03	2.13E+00	8.97E-05	1.56E-01	0.00E+00	6.67E-04	0.00E+00	4.88E-05
Pennsylvania (PA)	2,838	1.86E-03	1.42E+00	1.36E-04	1.04E-01	0.00E+00	9.16E-03	0.00E+00	6.70E-04
Texas (TX)	32,780	8.80E-04	2.11E+00	6.44E-05	1.55E-01	2.09E-09	3.02E-03	1.53E-10	2.21E-04
West Virginia (WV)	549	1.37E-04	1.68E+00	1.00E-05	1.23E-01	0.00E+00	7.92E-03	0.00E+00	5.79E-04
Wyoming (WY)	1,302	8.32E-03	1.29E+00	6.09E-04	9.42E-02	3.57E-11	2.01E-04	2.61E-12	1.47E-05

[a] 50th percentile in well risks calculated by average air concentration;
[b] 99th percentile in well risks calculated by maximum air concentration.
NA: not available.

Table 5-4. Potential acute and chronic exposures for non-cancer and cancer risks based on maximum air concentrations at each well are listed.

State	Num. of Wells	Risks [a]		Num. of Wells		
		Min	Max	1< risk <=5	5< risk <=10	10< risk
Acute exposure for non-cancer risk						
AR	504	1.00	22.56	445	38	21
CA	30	1.03	8.69	27	3	0
CO	82	1.01	4.57	82	0	0
KS	51	1.01	5.36	50	1	0
LA	120	1.03	22.41	85	21	14
MT	16	1.01	5.79	14	2	0
ND	492	1.00	20.39	474	15	3
NM	144	1.00	5.79	141	3	0
OH	46	1.04	4.85	46	0	0
OK	641	1.00	45.49	621	13	7
PA	171	1.00	28.70	160	6	5
TX	5,171	1.00	31.64	4,748	326	97
WV	15	1.00	3.58	15	0	0
WY	44	1.03	8.23	41	3	0
Total	7,527	1.00	45.49	6,949	431	147
Chronic exposure for non-cancer risk						
AR	6	1.04	1.65	6	0	0
LA	8	1.02	1.64	8	0	0
ND	1	1.49	1.49	1	0	0
OK	7	1.00	3.33	7	0	0
PA	2	1.14	2.10	2	0	0
TX	41	1.00	2.32	41	0	0
Total	65	1.00	3.33	65	0	0
				10^{-6}< risk <=10^{-4}	10^{-4}< risk <=10^{-2}	10^{-2}< risk
Acute exposure for cancer risk						
AR	1	1.10E-04	1.10E-04	0	1	0
CA	17	3.38E-06	2.36E-04	16	1	0
CO	319	1.03E-06	4.44E-02	254	63	2
KS	34	1.96E-06	1.82E-03	28	6	0
LA	61	1.07E-06	5.23E-02	15	45	1
MT	56	2.29E-06	2.45E-02	27	28	1
ND	367	1.19E-06	6.16E-01	273	62	32
NM	536	1.01E-06	3.93E-02	383	149	4
OH	51	1.71E-05	2.96E-02	12	36	3
OK	234	1.02E-06	5.89E-02	143	79	12
PA	344	1.47E-06	1.67E-02	140	200	4
TX	2,460	1.00E-06	9.43E-01	1,560	859	41
WV	41	2.91E-05	8.15E-03	1	40	0
WY	46	1.44E-06	2.36E-02	40	5	1
Total	4,567	1.00E-06	9.43E-01	2,892	1,574	101
Chronic exposure for cancer risk						
AR	1	8.03E-06	8.03E-06	1	0	0
CA	15	1.04E-06	1.72E-05	15	0	0
CO	237	1.00E-06	3.25E-03	231	6	0
KS	14	1.00E-06	1.33E-04	13	1	0
LA	56	2.91E-06	3.83E-03	55	1	0
MT	46	1.06E-06	1.79E-03	44	2	0
ND	279	1.01E-06	4.51E-02	231	40	8
NM	363	1.00E-06	2.88E-03	309	54	0
OH	51	1.25E-06	2.16E-03	42	9	0
OK	154	1.02E-06	4.31E-03	120	34	0
PA	336	1.07E-06	1.23E-03	298	38	0
TX	1,908	1.01E-06	6.90E-02	1,734	171	3
WV	41	2.13E-06	5.96E-04	18	23	0
WY	17	1.19E-06	1.73E-03	15	2	0
Total	3,518	1.00E-06	6.90E-02	3,126	381	11

[a] the largest risk among all the receptors at each well.

Table 5-6 shows the organic compounds that pose the various risks based on their maximum air concentrations and the radii from 5 to 180 m for each well. For the non-cancer exposure risks, there were 8 organic compounds with acute exposure for non-cancer risks from 1.00 to 45.49 in 7,460 wells. Of the 7,460 wells 7,282 wells of contained methanol with the acute exposure for non-cancer risks (>1) and 6,894 wells had the acute exposure for non-cancer risks between 1 and 5. This indicates that methanol was the major organic compound with a potential acute exposure for non-cancer risk in the hydraulic fracturing wells. There were 4 organic compounds with the chronic exposure for non-cancer risks between 1.00 and 3.33 in 65 wells. For the cancer exposure risks, there were 8 organics with the acute exposure for cancer risks greater than 10^{-6} in 4,566 wells, and 7 organics with the chronic exposure for cancer risks ($>10^{-6}$) in 3,516 wells. Among these organic compounds formaldehyde posed the acute exposure for cancer risk, which ranged from 1.00×10^{-6} to 0.94 in 4,267 wells, and the chronic exposure for cancer risks from1.00×10^{-6} to 6.92×10^{-2} in 3,470 wells. This suggests that formaldehyde was the dominant contributor to both the acute exposure for cancer risk and the chronic exposure for cancer risks in hydraulic fracturing wells.

Benzene was reported to be a major contributor to the chronic exposure for cancer risk in hydraulic fracturing by McKenzie et al. (2012). Their study found the chronic exposure for cancer risk due to benzene based on the median concentrations was 3.03×10^{-6} for distances > 0.5 mile and 3.33×10^{-6} for distances ≤ 0.5 mile, which contributed to 84% and 67%, respectively, of the total cancer exposure risks calculated using four organic compounds 1,3-butadiene, benzene, ethylbenzene, and styrene. The study presented here shows the chronic exposure for cancer risks from benzene based on the maximum concentrations at the radial distances ranging from 5 to 180 m were between 2.08×10^{-6} and 3.19×10^{-5} for 10 wells, which were the total number of wells with additives containing this compound. Comparing the wells associated with the estimated acute exposure for non-cancer risks (>1) (7,527 wells), the chronic exposure for non-cancer risks (>1) (65 wells), the acute exposure for cancer risks ($>10^{-6}$) (4,567 wells), and the chronic exposure for cancer risks ($>10^{-6}$) (3,518 wells) from this study showed that there were 7,460, 65, 4,566, and 3,516 wells that had at least one organic compound that had an acute exposure for non-cancer risk (>1), a chronic exposure for non-cancer risk (>1), an acute exposure for cancer risk ($>10^{-6}$), and a chronic exposure for

cancer risk (>10^{-6}), respectively. These values indicated that the hydraulic fracturing wells, whose risks were related to the emissions from the chemical storage tanks were due to the organic compounds with risks higher than 1 or 10^{-6}, rather than the combination risks associated with more than one organic compound with risks less than 1 or 10^{-6}.

5.4.3. Combined Inhalation Exposures

In Figure 5-1 (and Table A-36 in the Appendix D) shows the air concentrations caused by the emissions from the open flowback pits reported in Bloomdahl et al. (2014) and calculated in this study by the AP-42 Chapter 4.3 coupled with AERMOD under the same conditions. The box model (Equation A-40 in the Appendix D) was used in Bloomdahl et al. (2014) to calculate the air concentrations based on emissions from the open flowback pits by the stagnant two-film modes (Equation A-39 in the Appendix D). Air concentrations estimated by the AP-42 Chapter 4.3 and AERMOD were around 13.84% (median) lower than those estimated by the stagnant two-film model and the box model (Figure 5-1), although the median emissions by the AP-42 Chapter 4.3 were around 11.23% higher than those by the stagnant two-film model. The box model assumes the air mass inside the box is well mixed (Colls and Tiwary, 2009; Gurjar et al., 2010), while the Gaussian dispersion model (Equation A-38 in the Appendix D) used in AERMOD assume the air concentration has a Gaussian distribution in either the crosswind or the vertical directions (De Visscher, 2013). This may explain the lower air concentrations estimated using AERMOD than those established with the Box model under the same simulation conditions. When using the meteorological data from the closest observation stations to the 4,270 hydraulic fracturing wells located in the Marcellus Shale, the median air concentrations calculated using the AP-42 Chapter 4.3 and AERMOD were around 67.03% of the values estimated by the stagnant two-film model and the box model with the meteorological conditions used in the study performed by Bloomdahl et al. (2014). For the air concentrations from the open flowback pits nearest these wells, the meteorological data from the nearest observation stations were used to run AERMOD based on emissions calculated by the AP-42 Chapter 4.3.

Table 5-5. Potential inhalation risks caused by organic chemicals in storage tanks used for hydraulic fracturing within a 5 m radius of each well are listed.

Substance Name	CASRN	Non-cancer				Cancer			
		Acute		Chronic		Acute		Chronic	
		50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]	50th in Aver. [a]	99th in Max. [b]
Acetaldehyde	75-07-0	0.00E+00	2.52E+00	0.00E+00	1.85E-01	NA	NA	NA	NA
Acrylamide	79-06-1	0.00E+00	1.67E-03	0.00E+00	1.22E-04	0.00E+00	1.00E-06	0.00E+00	7.34E-08
Acrylic acid	79-10-7	8.63E-01	2.24E+01	6.32E-02	1.64E+00	NA	NA	NA	NA
Acrylonitrile	107-13-1	8.88E-01	8.11E+00	6.50E-02	5.94E-01	1.21E-04	1.10E-03	8.83E-06	8.07E-05
Aniline	62-53-3	0.00E+00	7.46E-02	0.00E+00	5.46E-03	NA	NA	NA	NA
Benzene	71-43-2	1.37E-01	1.86E+00	1.00E-02	1.36E-01	3.21E-05	4.36E-04	2.35E-06	3.19E-05
Bis(chloroethyl)ether	111-44-4	NA	NA	NA	NA	0.00E+00	1.25E-04	0.00E+00	9.17E-06
Cumene	98-82-8	2.88E-07	2.00E-03	2.11E-08	1.47E-04	NA	NA	NA	NA
Dichloromethane	75-09-2	1.69E-04	1.38E-03	1.24E-05	1.01E-04	1.02E-09	8.27E-09	7.43E-11	6.05E-10
1,3-Dichloropropene	542-75-6	1.73E-04	1.18E-03	1.26E-05	8.60E-05	1.38E-08	9.40E-08	1.01E-09	6.88E-09
N,N-Dimethylformamide	68-12-2	0.00E+00	4.06E-02	0.00E+00	2.97E-03	NA	NA	NA	NA
1,4-Dioxane	123-91-1	0.00E+00	3.86E-02	0.00E+00	2.82E-03	0.00E+00	5.78E-06	0.00E+00	4.23E-07
Epichlorohydrin	106-89-8	1.45E-03	1.42E+01	1.06E-04	1.04E+00	1.74E-09	1.70E-05	1.27E-10	1.25E-06
Ethylbenzene	100-41-4	4.80E-05	3.15E-02	3.52E-06	2.31E-03	NA	NA	NA	NA
2-Butoxyethanol	111-76-2	3.02E-07	6.59E-04	2.21E-08	4.82E-05	NA	NA	NA	NA
Formaldehyde	50-00-0	NA	NA	NA	NA	3.29E-06	4.77E-03	2.41E-07	3.49E-04
Methanol	67-56-1	3.37E-03	2.31E+00	2.47E-04	1.69E-01	NA	NA	NA	NA
Methyl isobutyl ketone	108-10-1	7.24E-07	5.84E-04	5.30E-08	4.27E-05	NA	NA	NA	NA
Naphthalene	91-20-3	2.77E-07	4.82E-03	2.03E-08	3.53E-04	NA	NA	NA	NA
Propylene glycol monomethyl ether	107-98-2	6.65E-05	2.96E-03	4.87E-06	2.17E-04	NA	NA	NA	NA
Propylene oxide	75-56-9	3.45E-03	2.84E-02	2.52E-04	2.08E-03	3.82E-07	3.16E-06	2.80E-08	2.31E-07
Toluene	108-88-3	1.85E-06	2.94E-03	1.35E-07	2.15E-04	NA	NA	NA	NA
Xylenes	1330-20-7	3.19E-06	3.44E-01	2.34E-07	2.52E-02	NA	NA	NA	NA

[a] 50th percentile in organic risks calculated by average air concentration.
[b] 99th percentile in organic risks calculated by maximum air concentration.
NA: not available.

Table 5-6. Organic compounds that pose potential acute and chronic non-cancer and cancer exposure risks based on maximum air concentrations at each well are listed.

Substances	CASRN	Num. of Wells	Risks [a]		Num. of Wells		
			Min	Max	1< risk <=5	5< risk <=10	10< risk
Acute exposure for non-cancer risk							
Epichlorohydrin	106-89-8	8	1.48	19.47	2	5	1
Acrylonitrile	107-13-1	5	4.19	8.36	1	4	0
Xylenes	1330-20-7	3	1.20	1.45	3	0	0
Methanol	67-56-1	7,282	1.00	45.49	6,769	404	109
N,n-dimethylformamide	68-12-2	4	1.08	2.24	4	0	0
Benzene	71-43-2	3	1.01	1.86	3	0	0
Acetaldehyde	75-07-0	96	1.00	27.45	80	8	8
Acrylic acid	79-10-7	67	1.35	37.64	34	8	25
Total [b]		7,460	1.00	45.49	6,894	429	143
Chronic exposure for non-cancer risk							
Epichlorohydrin	106-89-8	1	1.42	1.42	1	0	0
Methanol	67-56-1	47	1.00	3.33	47	0	0
Acetaldehyde	75-07-0	5	1.22	2.01	5	0	0
Acrylic acid	79-10-7	12	1.00	2.75	12	0	0
Total [b]		65	1.00	3.33	65	0	0
					10^{-6}< risk <=10^{-4}	10^{-4}< risk <=10^{-2}	10^{-2}< risk
Acute exposure for cancer risk							
Epichlorohydrin	106-89-8	8	1.77E-06	2.34E-05	8	0	0
Acrylonitrile	107-13-1	5	5.69E-04	1.14E-03	0	5	0
Dichloroethyl ether	111-44-4	7	5.35E-06	3.28E-04	4	3	0
Dioxane	123-91-1	208	1.00E-06	5.99E-05	208	0	0
Formaldehyde	50-00-0	4,267	1.00E-06	9.43E-01	2,606	1,560	101
Benzene	71-43-2	10	2.84E-05	4.36E-04	4	6	0
Propylene oxide	75-56-9	7	1.29E-06	3.16E-06	7	0	0
Residual acrylamide	79-06-1	98	1.02E-06	6.68E-05	98	0	0
Total [b]		4,566	1.00E-06	9.43E-01	2,912	1,574	101
Chronic exposure for cancer risk							
Epichlorohydrin	106-89-8	1	1.71E-06	1.71E-06	1	0	0
Acrylonitrile	107-13-1	5	4.17E-05	8.32E-05	5	0	0
Dichloroethyl ether	111-44-4	6	1.20E-06	2.40E-05	6	0	0
Dioxane	123-91-1	14	1.01E-06	4.38E-06	14	0	0
Formaldehyde	50-00-0	3,470	1.00E-06	6.90E-02	3,078	381	11
Benzene	71-43-2	10	2.08E-06	3.19E-05	10	0	0
Acrylamide	79-06-1	10	1.84E-06	4.89E-06	10	0	0
Total [b]		3,516	1.00E-06	6.90E-02	3,124	381	11

[a] the largest risk among all the receptors at each well.
[b] the total well number may be lower than the sum of the well numbers due to the fact more than one organic species coexisted in more than one well.

The median inhaled risks based on the average air concentrations at a certain distance and the 97.5th percentile inhaled risks based on the maximum air concentrations at a certain distance from the open flowback pits and the chemical storage tanks are shown in Table A-37 (in the Appendix D). The combined non-cancer exposure risks are presented in Figure 5-2.(a-d). With the distance from 5 to 180 m, the median non-cancer risks for the acute (Figure 5-2.a) and chronic (Figure 5-2.c) exposures, and the 97.5th percentile non-cancer risks for the chronic exposure (Figure 5-2.d) were less than 1, which are considered negligible (Lau et al., 2014). In Figure 5-2.b, the 97.5th percentile values for the acute exposure for non-cancer risks ranged from 0.52 to 4.64, which indicate that the receptors located at within the 5 and 180 m radial distances away from the open flowback pits and the chemical storage tanks may be exposed to adverse risks. The exposures to these risks were mainly attributed to the open flowback pits, and existed within a distance of 80 m away from the open flowback pits or 20 m away from chemical storage tanks (Table A-37 in the Appendix D). The open flowback pits primarily contributed to the acute and chronic exposures for non-cancer risks.

The combined exposure for cancer risks from the open flowback pits and the chemical storage tanks are shown in Figure 5-2.(e-h). In Figure 5-2.e, the median values for the acute exposure for cancer risks ranged from 5.00×10^{-7} to 1.87×10^{-5}, indicating the receptors located at within the 5 m and 180 m radii are potentially exposed to cancer risks. Those risks occurred within the 120 m radius from the open flowback pits (Table A-37 in the Appendix D). In Figure 5-2.f, the 97.5th percentile values in the acute exposure for cancer risks were between 1.30×10^{-4} and 1.92×10^{-3}, indicating that the receptors located within the 180 m radius of the flowback pits have a potential to contribute to unacceptable acute exposures for cancer risk ($>10^{-4}$). For the chronic exposure for cancer risks, the median values were between 3.50×10^{-8} and 1.38×10^{-6} (Figure 5-2.g), and the 97.5th percentile values ranged from 9.50×10^{-6} to 1.40×10^{-4} (Figure 5-2.h). For both the acute and chronic exposures for cancer risks, the median risks were primarily dominated by the open flowback pits while major contributions for the 97.5th percentile risks were from the chemical storage tanks.

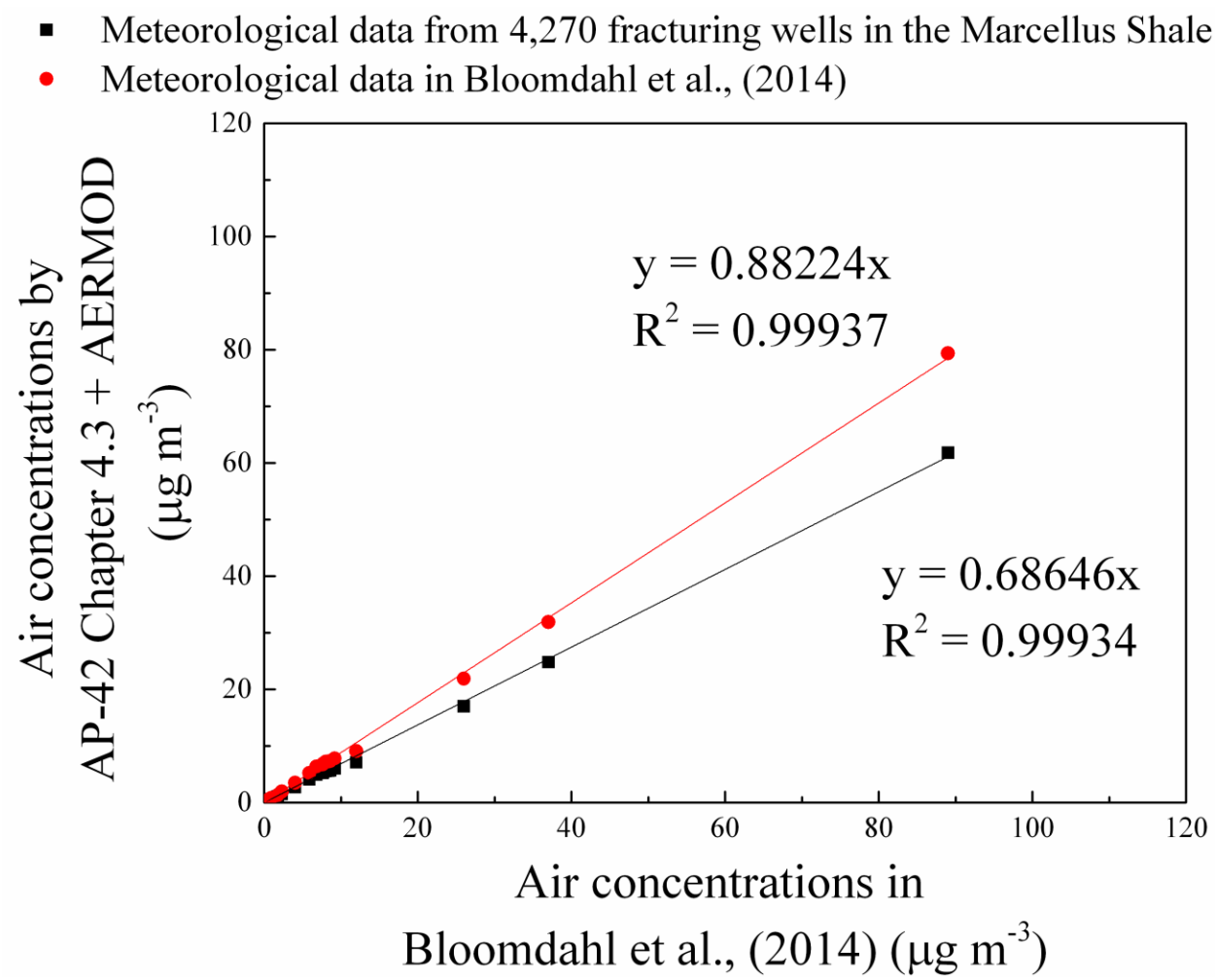

Figure 5-1. Estimated air concentrations from the open flowback pits using the AP-42 Chapter 4.3 + AERMOD and by the stagnant two-film model (Equation A-39 in the Appendix D) + the box model (Equation A-40 in the Appendix D) from the Bloomdahl et al. (2014). The data descriptions are shown in Table A-36 (in the Appendix D).

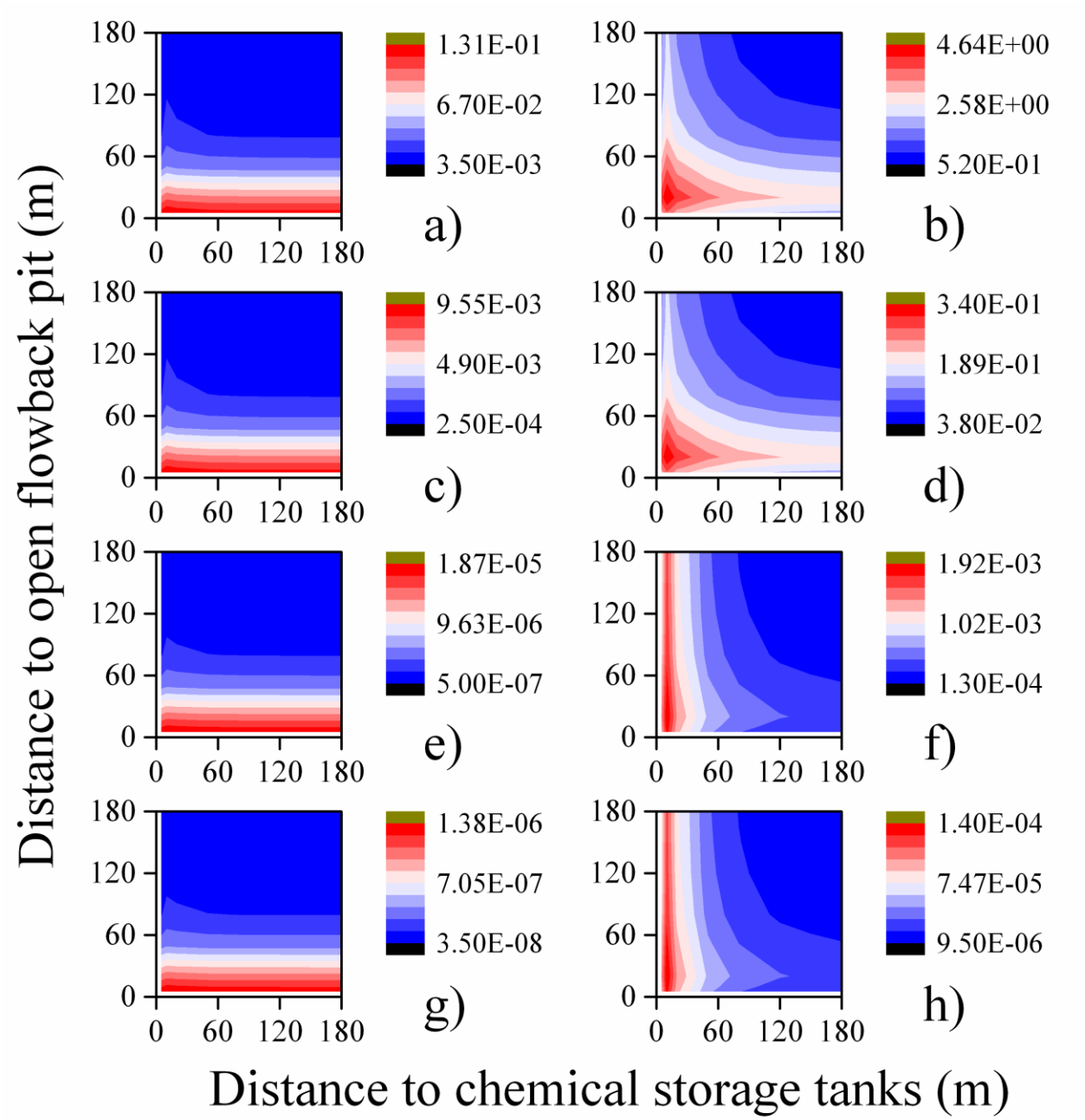

Figure 5-2. Inhaled risks associated with the combined emissions from the open flowback pits and chemical storage tanks: a) the 50th non-cancer risks for acute exposure; b) the 97.5th non-cancer risks for acute exposure; c) the 50th non-cancer risks for chronic exposure; d) the 97.5th non-cancer risks for chronic exposure; e) the 50th cancer risks for acute exposure; f) the 97.5th cancer risks for acute exposure; g) the 50th cancer risks for chronic exposure; and h) the 97.5th cancer risks for chronic exposure. The 50th percentile risks were calculated based on the average air concentrations, while the 97.5th percentile risks were obtained using the maximum air concentrations.

5.5. Conclusions

This study investigated the occupational inhalation exposures and associated risks of 23 organics in 60,644 hydraulic fracturing wells. The occupational inhalation exposure and associated risks were based on the air concentrations with the distances from 5 to 180 m away from the emission sources. The air concentrations were simulated using AERMOD based on emissions from chemical storage tanks and open flowback pits. Due to the overlapped air concentrations from the surrounding wells and the existing VOCs emissions for each well, the air concentrations based from chemical storage tanks and the associated inhalation risks in this study were expected to be lower than the field values. The air concentrations for the 23 organic compounds listed in this study were lower than the recommended exposure limits (RELs) suggested by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA).

This study shows percentage of wells with the possibilities of the acute exposure for non-cancer risks, chronic exposure for non-cancer risks, acute exposure for cancer risks, and chronic exposure for cancer risks on workers were 12.41%, 0.11%, 7.53%, and 5.80%, respectively. There were 8 organic compounds with acute exposure for non-cancer risks from 1.00 to 45.49, which were found to be used in the hydraulic fracturing chemicals of 7,460 wells. Methanol was the major contributor to the acute exposure for non-cancer risks between 1.00 and 45.49 in 7,282 hydraulic fracturing wells. Eight organic compounds contributed to the acute exposure for cancer risks ($>10^{-6}$) in 4,566 wells, and 7 organic compounds contributed to the chronic exposure for cancer risks ($>10^{-6}$) in 3,516 wells. Among those wells, formaldehyde was the dominant component that contributed to both the acute and chronic exposures for cancer risks ($>10^{-6}$) in 4,267 and 3,470 wells, respectively.

The combined median and 97.5th percentile risks caused by emissions from the open flowback pits and the chemical storage tanks were investigated within 5 m and 180 m distances away from these emissions sources. The 97.5th percentile values for the acute exposure for non-cancer risks ranged from 0.52 to 4.64 for different wells. The median and 97.5th percentile values for the acute exposure for cancer risks ranged

from 5.00×10^{-7} to 1.87×10^{-5}, and from 1.30×10^{-4} and 1.92×10^{-3}, respectively, for the different wells. For the chronic exposure for cancer risks, the median values were between 3.50×10^{-8} and 1.38×10^{-6}, and the 97.5th percentile values were from 9.50×10^{-6} to 1.40×10^{-4}. The 97.5th percentile acute and chronic exposures for cancer risks were dominated by the air concentrations and emissions from the chemical storage tanks while the other investigated risks were primarily associated with the open flowback pits.

CHAPTER 6

CONCLUSIONS AND FUTURE WORKS

6.1. Conclusions

This study estimated the inhaled exposures and associated risks on the workers in hydraulic fracturing wells caused by the storing and emptying operations on the chemical storage tanks. The general conclusions, which are related with the objectives and hypothesis of this study, are illustrated from the following four aspects.

6.1.1. Water usage for Mixing Chemical Additives to Make up the Hydraulic Fracturing Fluids in Hydraulic Fracturing

Approximately 930 Mm^3 of water were used to hydraulically fracture 80,047 wells during that time. Of the 930 Mm^3, the 40,521 wells put into production in Texas required approximately half the amount of water, followed by Pennsylvania with 1.09×10^8 m^3 for 5,127 wells. The percentage of freshwater used in hydraulic fracturing for each state was relatively lower than the amount of water used by other industries, including agricultural irrigation and thermoelectric power. Of the 80,047 wells in this study, only 6,221 reported recycled wastewater volumes as part of their hydraulic fracturing fluids, which is less than 10% of the wells put into production at the time of this study. In a number of states, there was no recycling of the wastewater reported suggesting that this measure has yet to be adopted due to the low volumes of produced/flowback water returning and the high cost in treatments for recycling.

6.1.2. Profiles of Chemical Additives Used in Hydraulic Fracturing

For 5,071 wells fractured from September 2008 to August 2014 in Pennsylvania and West Virginia, there were 517 chemicals added into the hydraulic fracturing fluids. Of 517 chemicals, 96 were inorganic compounds, 358 were organic compounds, and the left 63 cannot be identified. Organics were added into 5,070 wells with a frequency of 68,555, while organics containing oxygen existed in 5,062 wells with a frequency of 52,181. Many toxic chemicals have been added into the hydraulic fracturing fluids, some of which are carcinogenic. Although most of chemicals occurring in the hydraulic fracturing fluids can be removed when adopting the appropriate treatments, some chemicals are persistent. Besides, the degradation of some chemicals would produce more toxic and persistent degradation byproducts. Moreover, the

biocides and disinfectants occurring in the hydraulic fracturing are capable of inhibiting the degradation of microorganisms.

6.1.3. Potential Emissions from Chemical Storage Tanks in Hydraulic Fracturing

The median emission was 0.221 kg d^{-1} per well for the 72,023 hydraulic fracturing wells. The main contributor to the emissions from chemical storage tanks in hydraulic fracturing wells was non-methane volatile organic compounds (NMVOCs). The median well emission was 0.110 kg per well in 2008 and 0.786 kg per well in 2014, which shows an increasing trend. The increase in well emissions was induced by the growth tendencies in volumes of chemical additives in each well, instead of emissions per cubic meter chemical additives. There were 17 organics listed in the 13th Report on Carcinogens (NTP, 2014), including benzene, oxirane, and formaldehyde are known human carcinogens, while the other 14 organics are considered or anticipated to be carcinogenic. There were 73 organics (including 60 NMVOCs and 13 NVOCs) found in the 2011 Agency Toxic Substances & Disease Registry (ATSDR) list, 15 (including 14 NMVOCs and 1 NVOCs) of which were in the Priority List of Hazardous Substances. Of the total emissions caused by all NMVOCs, 95.14% were due to those 60 NMVOCs founded in the 2011 ATSDR list.

6.1.4. Inhaled Occupational Exposures Caused by Chemical Storage Tanks in Hydraulic Fracturing

Comparing with recommended exposure limits (RELs) suggested by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA), the air concentrations of the 23 toxic organics were smaller. However, there were 7,527, 65, 4,567, and 3,518 out of 60,644 wells with the possibilities of the acute exposure for non-cancer risks, chronic exposure for non-cancer risks, acute exposure for cancer risks, and chronic exposure for cancer risks on workers, although the well percentages of 12.41%, 0.11%, 7.53%, and 5.80% were not significant. There were 8 organics with the acute exposure for non-cancer risks from 1.00 to 45.49 in 7,460 wells. Among those 8 organics, methanol posed the acute exposure for non-cancer risks between 1.00 and 45.49 in 7,282 wells, and was the major organic causing the acute exposure for non-cancer risks in hydraulic fracturing wells. Eight organics had the acute exposure for cancer risks ($>10^{-6}$) in 4,566 wells, and 7 organics had the chronic exposure for cancer risks ($>10^{-6}$) in 3,516 wells. Among those wells, formaldehyde posed the acute and

chronic exposures for cancer risks (>10^{-6}) in 4,267 and 3,470 wells, and was the dominant contributor to both the acute and chronic exposures for cancer risks in hydraulic fracturing wells.

6.2. Future Works

Although the potential health risks from hydraulic fracturing have been reviewed and summarized in the previous studies (Adgate et al., 2014; Shonkoff et al., 2014; Werner et al., 2015), the risk studies with the field or modeling data are few. It has been suggested that the studies about the effects of hydraulic fracturing on the exposure and health are urgently needed (Penning et al., 2014). Through a modeling approach, our study shows the storing and emptying of chemical additives posed the possibility of the inhaled health risks on workers standing with the distance of 5-180 m from chemical storage tanks at some hydraulic fracturing wells. For the future works and studies, the risks could be further investigated in the following aspects.

6.2.1. Epidemiological studies

Until now, there were few epidemiological studies about the adverse health effects on the communities caused by hydraulic fracturing. McKenzie et al. (2014) reported the prevalence of congenital heart defects and neural tube defects was related with the number and distance of natural gas wells within the radius of 10 miles. Rabinowitz et al. (2015) reported the prevalence of health symptoms were associated with the distance to the nearest natural gas well. The epidemiological studies about the workers in hydraulic fracturing wells have not yet been investigated and reported.

6.2.2. Source Apportionment for Air Pollutions

In order to reduce the adverse effects of air pollutions on the human health, it is important to have a good understand about the contribution of each emission source on the health exposure and also associated risks. Source apportionment is a technique for evaluating the impact of emissions from various sources (Viana et al., 2008). Beside the source of chemical storage tanks reported in this study, other VOCs emission sources would also have the possibility to pose the inhaled health risks. Bloomdahl et al. (2014) assessed the inhaled risks caused by VOCs emitted from the open flowback pits in hydraulic fracturing wells in Marcellus Shale. Esswein et al. (2014) monitored the field air concentrations during flowback operations

in six hydraulic fracturing wells, and found benzene concentrations sometimes exceeded the Occupational Safety and Health (NIOSH) recommended exposure limits (RELs). Beside toxic VOCs, the respirable crystalline silica dust created by mechanic handling of fracturing sands is considered as another identified inhaled risk substance (Esswein et al., 2013). The contributions of each emission source on the health exposure and associated risks have not been investigated and reported.

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APPENDICES

SUPPLEMENTARY INFORMATION

Appendix A

Table A-1. Summary of the information for the database used for the study.

State	Last Acquired Date (yyyy/mm/dd)	Num. of downloaded files (.pdf)	Num. of observations	Num. of imported file (.xlsx)	Num. of Wells
AR	2015/01/06	2,516	53,409	2,515	2,507
CA	2015/01/05	2,148	59,528	1,956	1,923
CO	2015/01/07	8,988	238,251	8,010	7,978
KS	2015/01/05	559	15,375	544	540
LA	2015/01/05	1,544	43,140	1,388	1,381
MT	2015/01/05	519	17,457	476	467
ND	2015/01/07	6,912	218,885	5,987	5,919
NM	2015/01/06	2,450	99,272	2,315	2,300
OH	2015/01/05	850	31,887	845	838
OK	2015/01/07	7,152	222,917	6,874	6,765
PA	2015/03/18	5,333	114,117	5,294	5,222
TX	2015/01/12	44,314	1,472,193	40,947	40,533
WV	2015/03/18	1,040	29,456	1,040	1,034
WY	2015/01/06	3,049	77,174	2,777	2,757
Total		87,374	2,693,061	80,968	80,164

Table A-2. Distribution of wells between 2008 and 2014.

State	Year							Total
	2008	2009	2010	2011	2012	2013	2014	
AR	0	0	1	827	692	517	470	2,507
CA	0	0	0	90	416	833	584	1,923
CO	0	0	63	2,544	1,959	1,743	1,669	7,978
KS	0	0	0	20	144	215	160	539
LA	0	0	4	657	285	228	207	1,381
MT	0	0	0	48	149	155	115	467
ND	0	1	5	535	1,262	1,976	2,140	5,919
NM	0	1	0	460	625	692	522	2,300
OH	0	0	0	12	137	302	387	838
OK	0	0	1	542	1,221	2,325	2,676	6,765
PA	2	20	57	1,180	1,395	1,255	1,218	5,127
TX	0	0	31	5,230	10,550	13,118	11,592	40,521
WV	0	0	7	115	218	316	370	1,026
WY	0	0	34	697	608	852	565	2,756
Total	2	22	203	12,957	19,661	24,527	22,675	80,047

Table A-3. Location of the Shale Plays in the United States.

Submodule regions	Shale plays	States	Shale gas [a] (trillion cubic feet)	Shale Oil [a] (billion barrels)
Northeast	Marcellus	Maryland, New York, Ohio, Pennsylvania, Virginia, West Virginia	410	N/A
	Antrim	Michigan	20	N/A
	Devonian Low Thermal Maturity	New York, Ohio, Pennsylvania, Tennessee, West Virginia	14	N/A
	New Albany	Illinois, Indiana, Kentucky	11	N/A
	Greater Siltstone	New York, Ohio, Pennsylvania, Virginia, West Virginia	8	N/A
	Big Sandy	Kentucky	7	N/A
	Cincinnati Arch	N/A	1	N/A
Gulf Coast	Haynesville	Texas, Louisiana	75	N/A
	Eagle Ford	Texas	21	3
	Floyd-Neal & Conasauga	Alabama, Mississippi	4	N/A
Mid-Continent	Fayetteville	Arkansas	32	N/A
	Woodford	Oklahoma	22	N/A
	Cana Woodford	Oklahoma	6	N/A
Southwest	Barnett	Texas	43	N/A
	Barnett-Woodford	Texas	32	N/A
	Avalon & Bone Springs	New Mexico, Texas	N/A	2
Rocky Mountain	Mancos	Colorado, Wyoming	21	N/A
	Lewis	Colorado, New Mexico	12	N/A
	Williston-Shallow Niobraran	N/A	7	N/A
	Hilliard-Baxter-Mancos	Colorado, Wyoming	4	N/A
	Bakken	North Dakota, Montana	N/A	4
West Coast	Monterey/Santos	California	N/A	15
		Total	750	24

Source: U.S. Energy Information Administration., 2011. Review of Emerging Resources: U.S. Shale Gas and Shale Oil Plays (U.S. Energy Information Administration, 2011); N/A: Not Available; [a] Undeveloped technically recoverable shale gas or oil estimated in Jan. 1, 2009.

Table A-4. Water use for hydraulic fracturing in the U.S reported in the previous studies.

Shale plays	Water use (Mm^3)	Number of Wells	References
Barnett (2000, 2011-mid)	145	~15,000	Nicot and Scanlon (2012)
Barnett (1981-2012)	210	N/A	Nicot et al. (2014)
Eagle Ford (2009-2013)	~150	8,301	Scanlon et al. (2014a)
Bakken (2005-2013)	~59.81	7,868	Scanlon et al. (2014a)

N/A: not available

Table A-5. The annual average water use per well in 14 states from 2008 to 2014 for wells where the amount of water used was reported. (Unit: m^3)

State	Year						
	2008	2009	2010	2011	2012	2013	2014
AR	0	0	16,640	19,161	19,871	19,213	18,903
CA	0	0	0	1,030	479	465	423
CO	0	0	7,250	4,307	6,207	10,662	13,012
KS	0	0	0	1,355	5,105	4,779	7,703
LA	0	0	21,984	20,321	19,080	21,077	23,474
MT	0	0	0	5,085	6,181	7,519	11,259
ND	0	281	10,854	6,966	8,434	10,221	13,366
NM	0	753	0	1,759	3,153	3,984	7,157
OH	0	0	0	21,366	16,261	21,328	31,988
OK	0	0	2,713	14,438	11,733	12,333	11,771
PA	15,256	12,213	15,674	17,103	16,466	22,045	30,252
TX	0	0	14,982	10,653	9,209	10,589	14,377
WV	0	0	12,695	19,576	20,087	27,484	41,337
WY	0	0	3,715	3,215	3,401	3,243	4,373

Table A-6. Water use per well reported in previous studies.

Regions	Water use per well (m^3)	References
Niobrara, CO (2012)	13,000	Vengosh et al. (2014)
Shale Plays in CO (2012)	6,207	This study
Marcellus	6,700-33,000 (average: 20,000)	Jiang et al. (2014)
Marcellus	7,700-38,000	Kargbo et al. (2010)
Eagle Ford (2009-2013)	~18,246	Scanlon et al. (2014a)
Shale Plays in Texas (2010-2014)	9,209-14,982	This study
Bakken (2005-2013)	~7,609	Scanlon et al. (2014a)
Shale Plays in Montana (2011-2014)	5,085-11,259	This study
Shale Plays in North Dakota (2010-2014)	6,966-13,366	This study
U.S. (2010-2013)	5,754 (median); 9,199 (mean)	Jackson et al. (2015)

Table A-7. Estimated water use in U.S. in 2010.

States	Public supply	Self-supplied domestic	Irrigation	Live-stock	Aquaculture	Self-supplied industrial	Mining	Thermoelectric power	Total
AR	1,148	53	220	37	82	793	28	11,399	15,613
CA	8,705	238	31,917	260	1,344	553	376	9,127	52,504
CO	1,172	52	13,416	51	169	180	39	106	15,198
KS	540	21	4,200	158	18	56	18	521	5,527
LA	1,031	65	1,282	11	430	2,846	16	6,123	11,800
MT	191	31	9,893	58	26	92	64	209	10,570
ND	95	5	228	30	8	26	37	1,156	1,589
NM	391	36	3,731	49	28	15	51	72	4,366
OH	1,893	189	73	33	47	676	159	9,976	13,043
OK	908	37	779	123	15	29	1,959	532	4,380
PA	1,962	278	37	72	149	1,197	86	7,447	11,233
TX	5,513	358	9,437	358	43	1,782	1,400	15,421	34,266
WV	261	44	0.12	7	72	1,061	21	3,413	4,877
WY	137	12	6,038	23	29	9	162	88	6,494

Unit: million cubic meters (Mm^3); Source: Table 2A in Maupin, M.A., Kenny, J.F., Hutson, S.S., Lovelace, J.K., Barber, N.L., Linsey, K.S., 2014. Estimated use of water in the United States in 2010: U.S. Geological Survey Circular 1405, p. 56.

Table A-8. Observation with the CAS No. in the CAS Number and with one of the following values in the Ingredients was assigned with "7732-18-5" in the CAS Number.

Ingredients
3% kcl water
3% nacl water
3% salt water
4% kcl water
4% nacl water
4% salt water
7% kcl water
2 kcl water
freshwater / sodium chloride
brine (nacl)

Table A-9. Observation without a CAS No. in the CAS Number and with one of the following values in the Ingredients was assigned with "7732-18-5" in the CAS Number.

Ingredients	Ingredients
1 kcl	fr-66 water
1% kcl water	fresh water
10% kcl water	fresh water with biocide
10% salt water	gelled (25#) 4% kcl water
15% salt water	h20
18% salt water	h20, naci
2% kcl water	h2o
3 nacl water	h2o + disolved salts
3% kcl water	h2o, naci
3% nacl	kcl water
3% nacl water	mix water
3% salt water	nacl water
4% brine (nacl)	salt water
4% kcl water	sodium chloride, water
4% nacl	water
4% nacl water	water (includes mix water supplied by client)
4% salt water	water (including mix water supplied by client)
5% kcl water	water (including mix water supplied by client) *
6% kcl water	water (including mix water supplied by client)*
6% salt water	water (including mix water supplied by client).
7% kcl water	water (including mix water supplied by clients)
brackish water	water (including mix water supplied by rosetta)*
brine (kcl)	water (including water supplied by client)
brine (nacl)	water (including water supplier by client)
brine (nacl) 4%	water (major)
brine volume	water (supplied by encana)
brine water	water and other inerts
carrier / base fluid - water	water and proprietary nonhazardous salt
carrier/bas fluid-water	water moisture
carrier/base fluid - water	water(including mix water supplied by client)*
cationic water	water, including mix water supplied by client
client supplied water	water, other
deionised water	water/proprietary non- hazardous salt
deionized water	water/salt

Table A-10. Recycled wastewater. Recycled wastewater was defined through the following two methods: 1) Observation with one of the following values in the Ingredient and with "7732-18-5" or empty value in the CAS Number were considered as recycled wastewater; 2) Observations with "7732-18-5" in the CAS Number and with "recycled" or "produced" in the variable of Ingredient, Trade Name, Purpose, or Comments were considered as recycled wastewater.

Ingredients
10# water frac g
15% hcl, wf125, yf125flexd, slickwater
20# waterfrac g
25# waterfac g
30# water frac g
30# waterfrac cmhpg
field salt water
field water
lease brine
lease crude
lease oil
lease salt water
lease water

Table A-11. Observation with the empty value in the CAS Number and one of the following values in the Ingredients was assigned with "7732-18-5" in the CAS Number.

Ingredients
water
h2o + disolved salts
mix water
water (including mix water supplied by client)*
recycled produced water
recycled water
fresh water
h2o
water, other

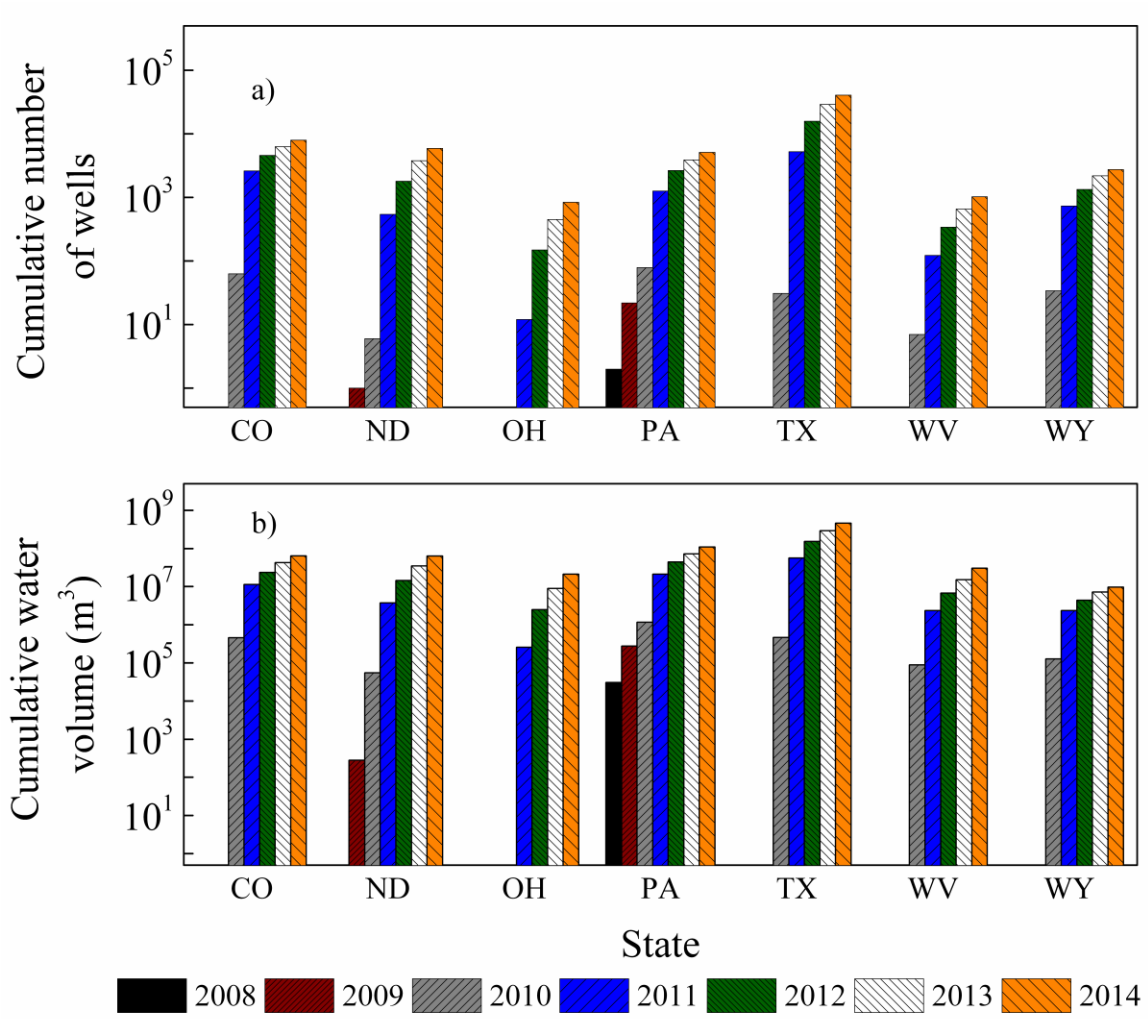

Figure A-1. Cumulative a) number wells and b) water volume for wells located in CO, ND, OH, PA, TX, WV, and WY.

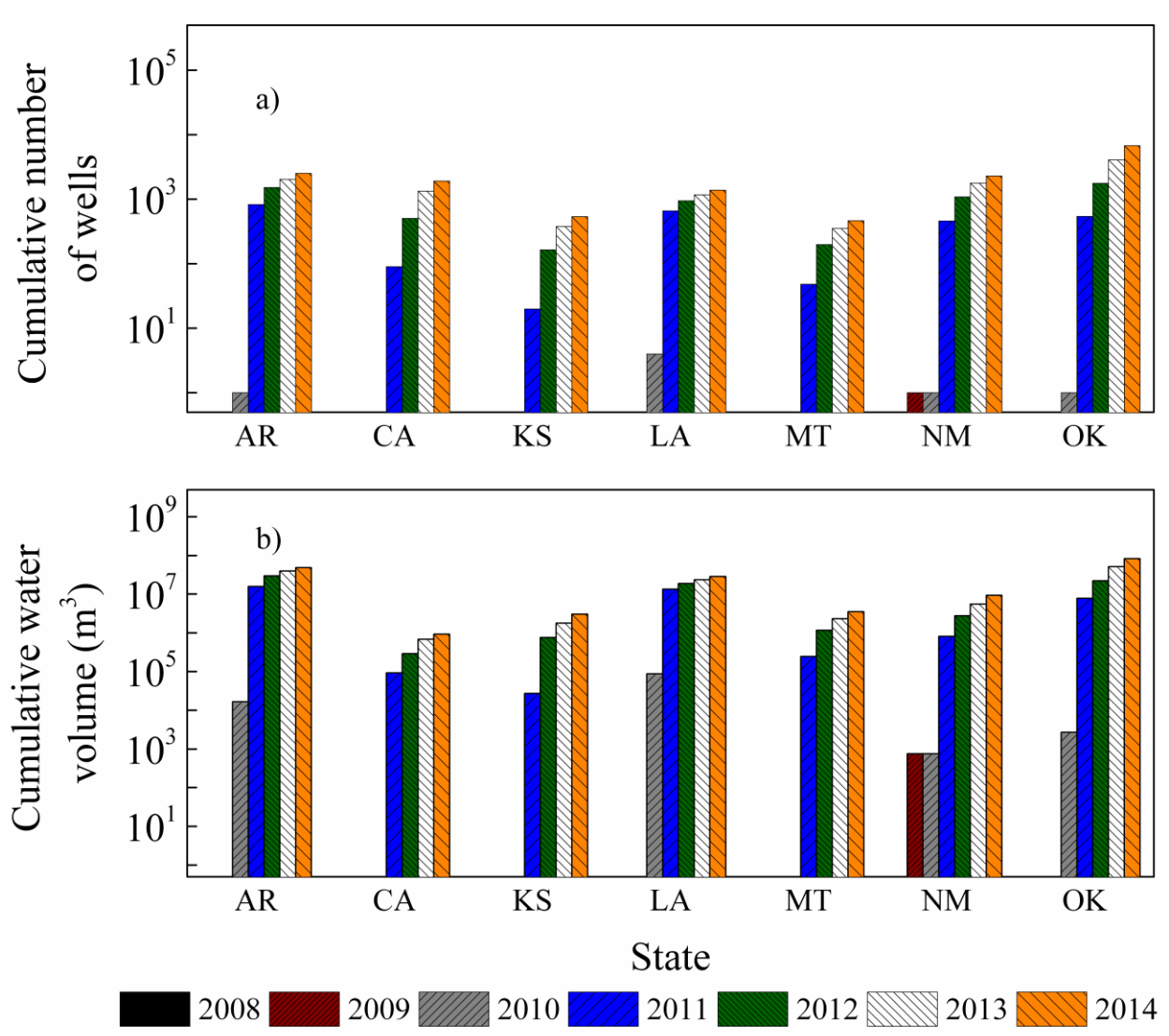

Figure A-2. Cumulative a) number of wells and b) volume of water used for wells located in AR, CA, KS, LA, MT, NM, and OK.

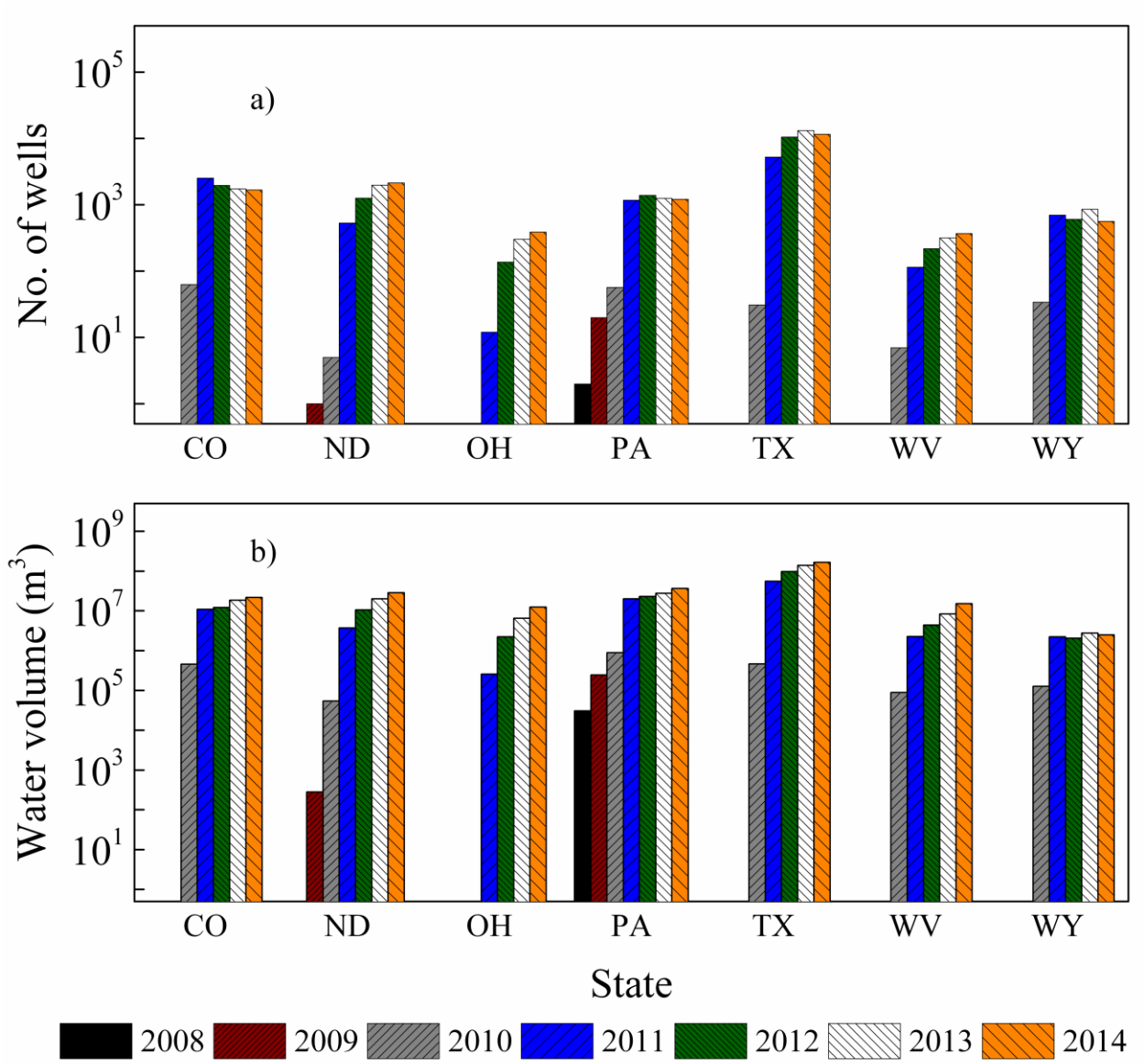

Figure A-3. The number of wells and the amount of water used per year to put the wells into production in CO, ND, OH, PA, TX, WV, and WY: a) Number of hydraulic fracturing wells; b) Water volumes.

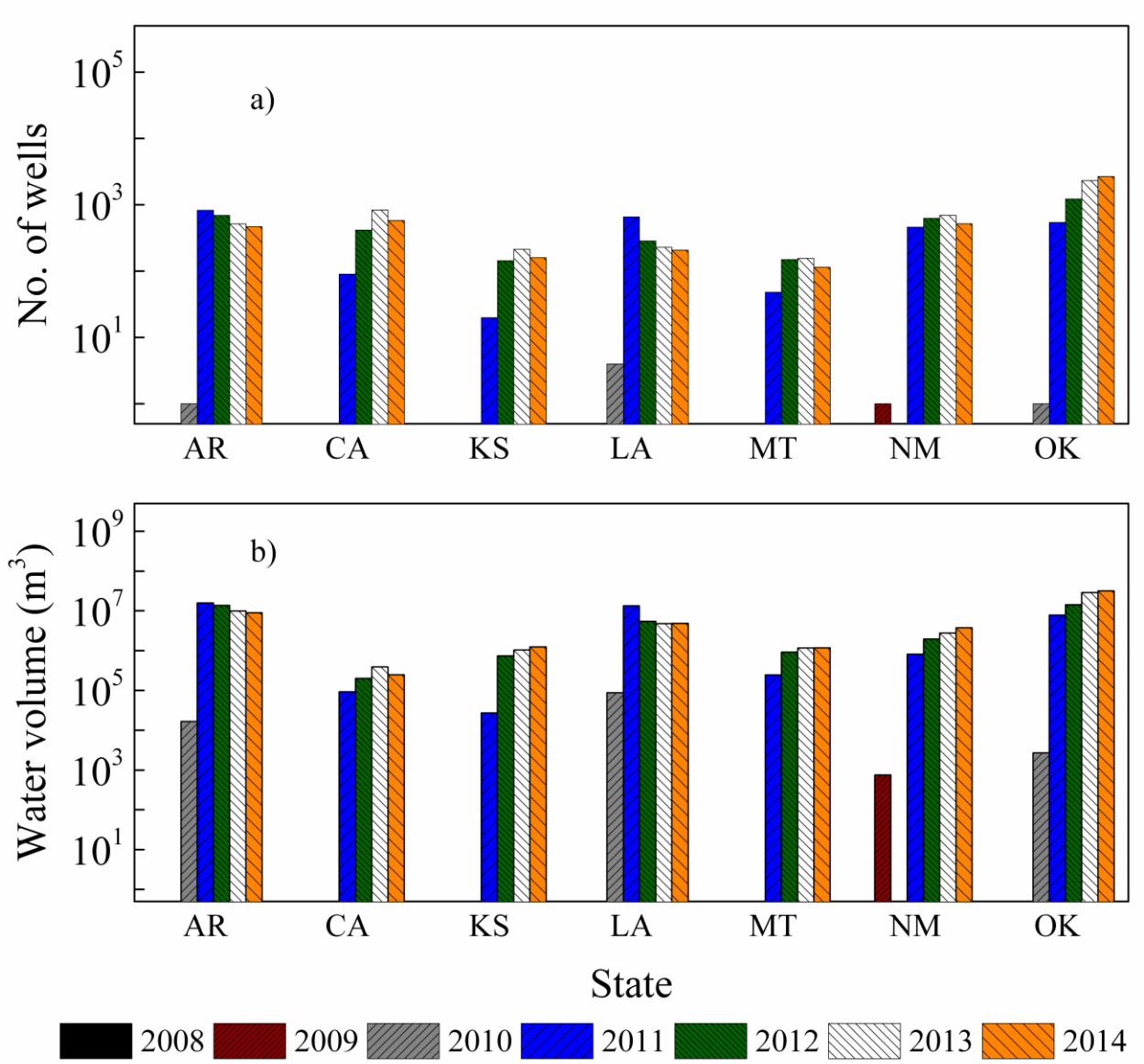

Figure A-4. The number of wells and the amount of water used per year to put the wells into production in AR, CA, KS, LA, MT, NM, and OK: a) Number of hydraulic fracturing wells; b) Water volumes.

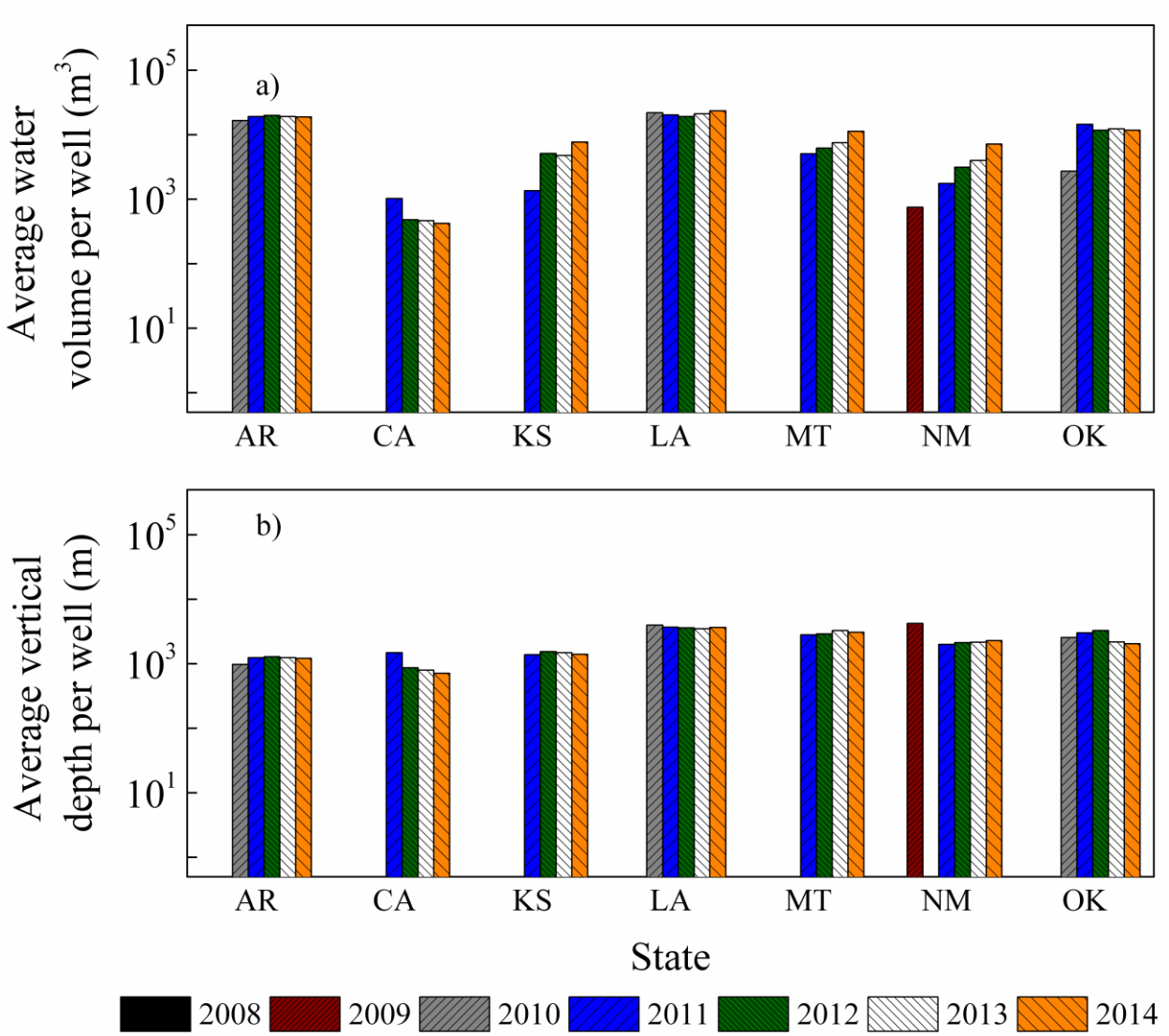

Figure A-5. The amount of water used per year to put the wells into production in AR, CA, KS, LA, MT, NM, and OK: a) Average water volumes per well in wells which reported the amounts of water use; b) Average vertical depth per well in wells which reported the vertical depths.

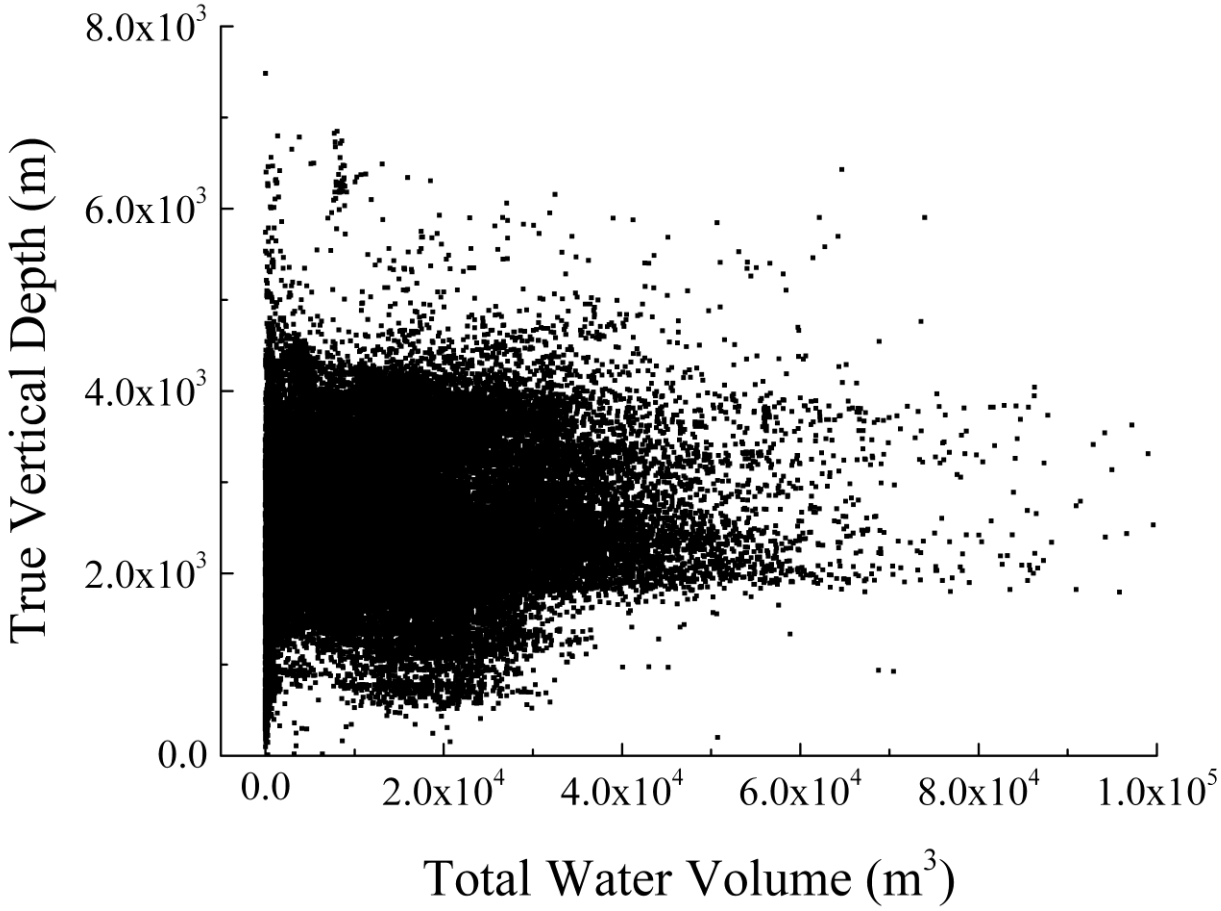

Figure A-6. Scatter plot of total water volume and vertical depth. Based on the data there is no linear relationship between vertical depth and water volume used for hydraulic fracturing of wells put into production.

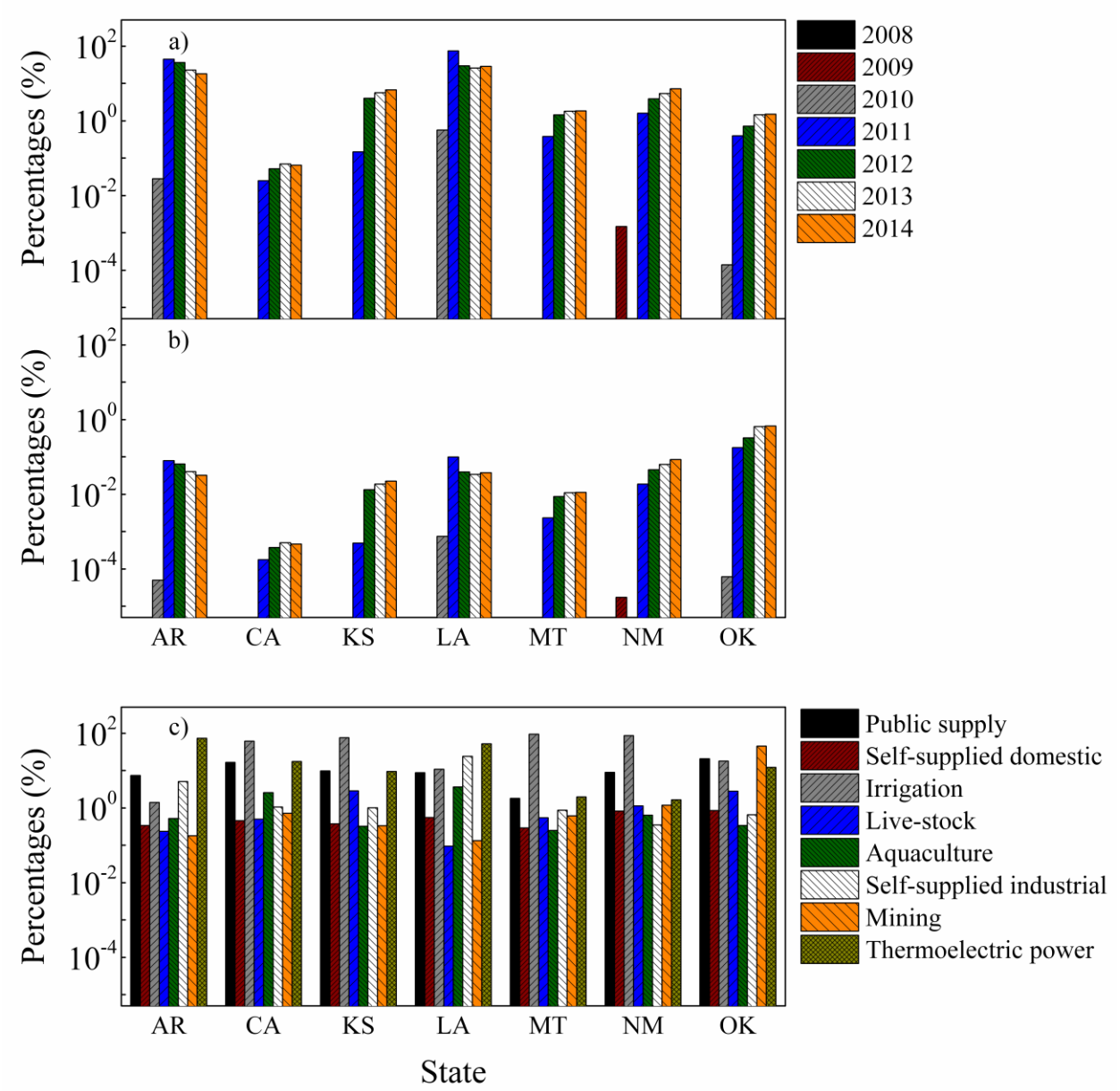

Figure A-7. Percentage of freshwater used in AR, CA, KS, LA, MT, NM, and OK: a) Hydraulic fracturing versus mining; b) Hydraulic fracturing versus total state water use; c) Water users versus total state water use.

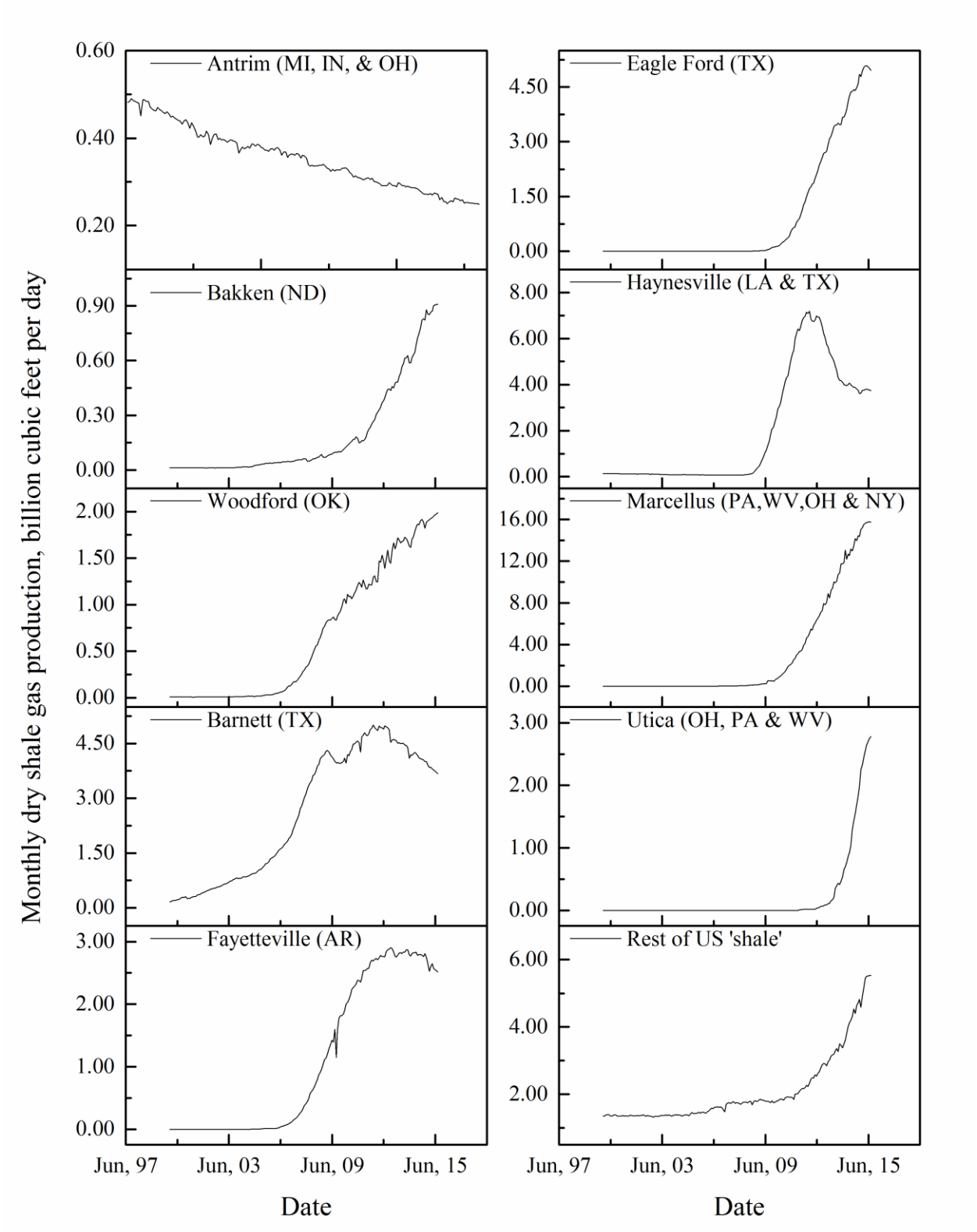

Figure A-8. Monthly dry shale gas production by shale plays from Jan 2000 to Aug 2015 (U.S. Energy Information Administration, 2015).

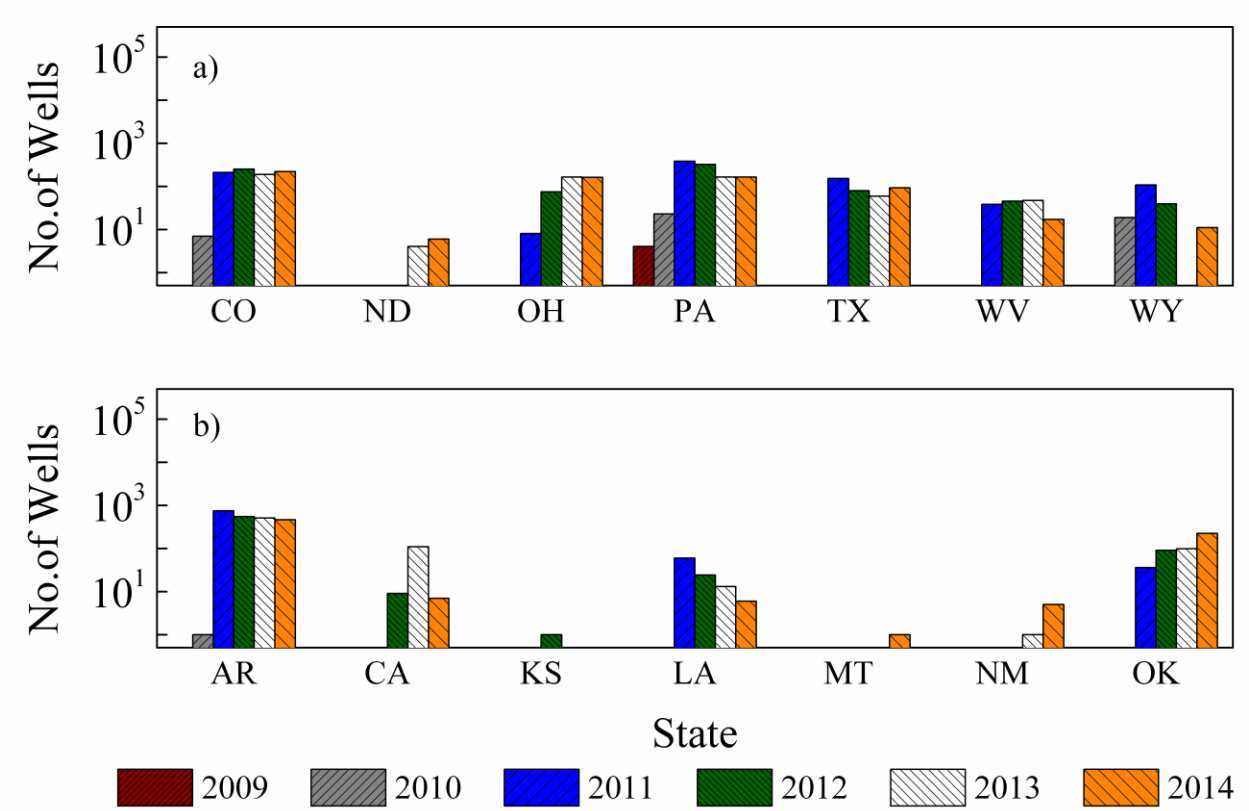

Figure A-9. Number wells where recycled wastewater was used for hydraulic fracturing fluids and volumes of recycled water for each state: a) CO, ND, OH, PA, TX, WV, and WY; b) AR, CA, KS, LA, MT, NM, and OK.

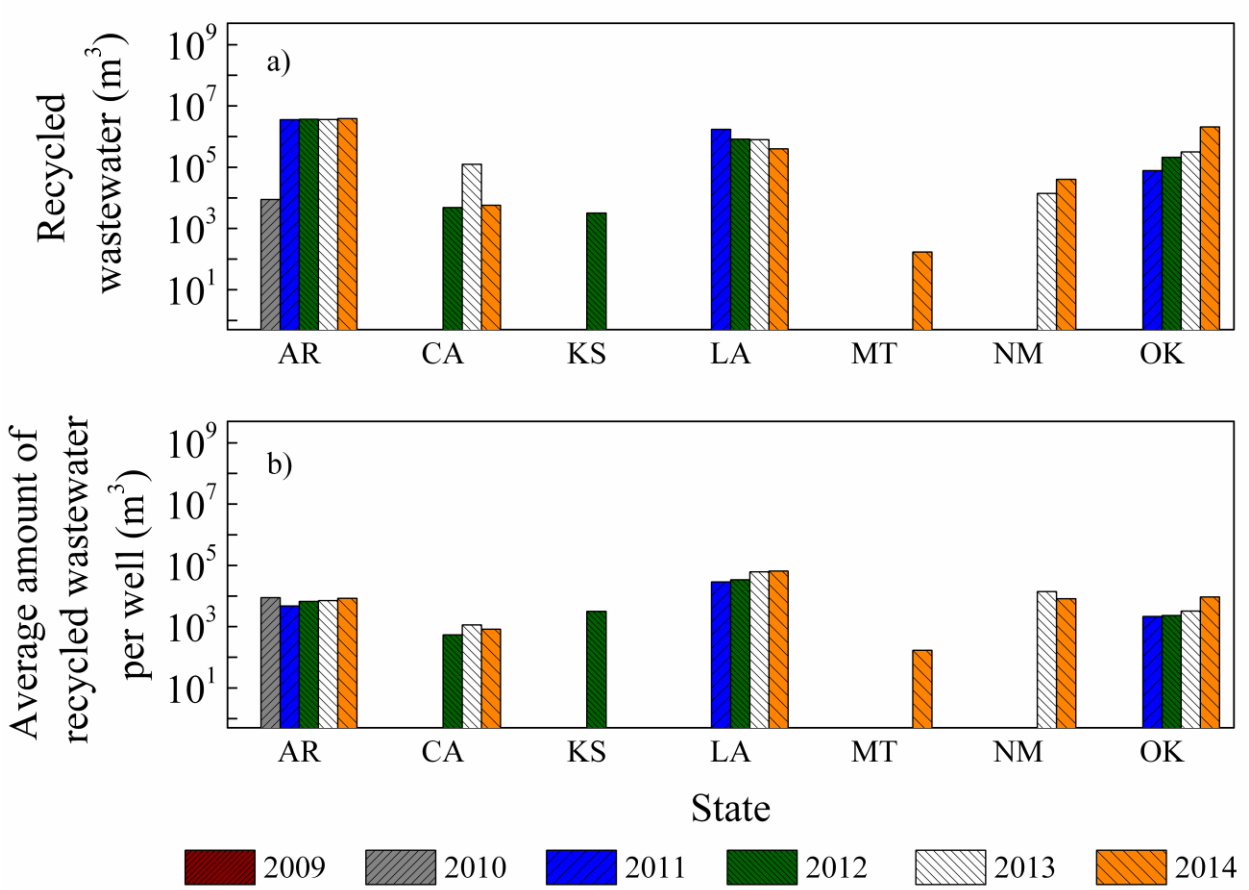

Figure A-10. Volumes of recycled water in wells where recycled wastewater was used for hydraulic fracturing fluids. a) Volume of recycled wastewater; b) Average amount of recycled wastewater per well reported to have recycled wastewater in the hydraulic fracturing fluid and the amounts of recycled wastewater.

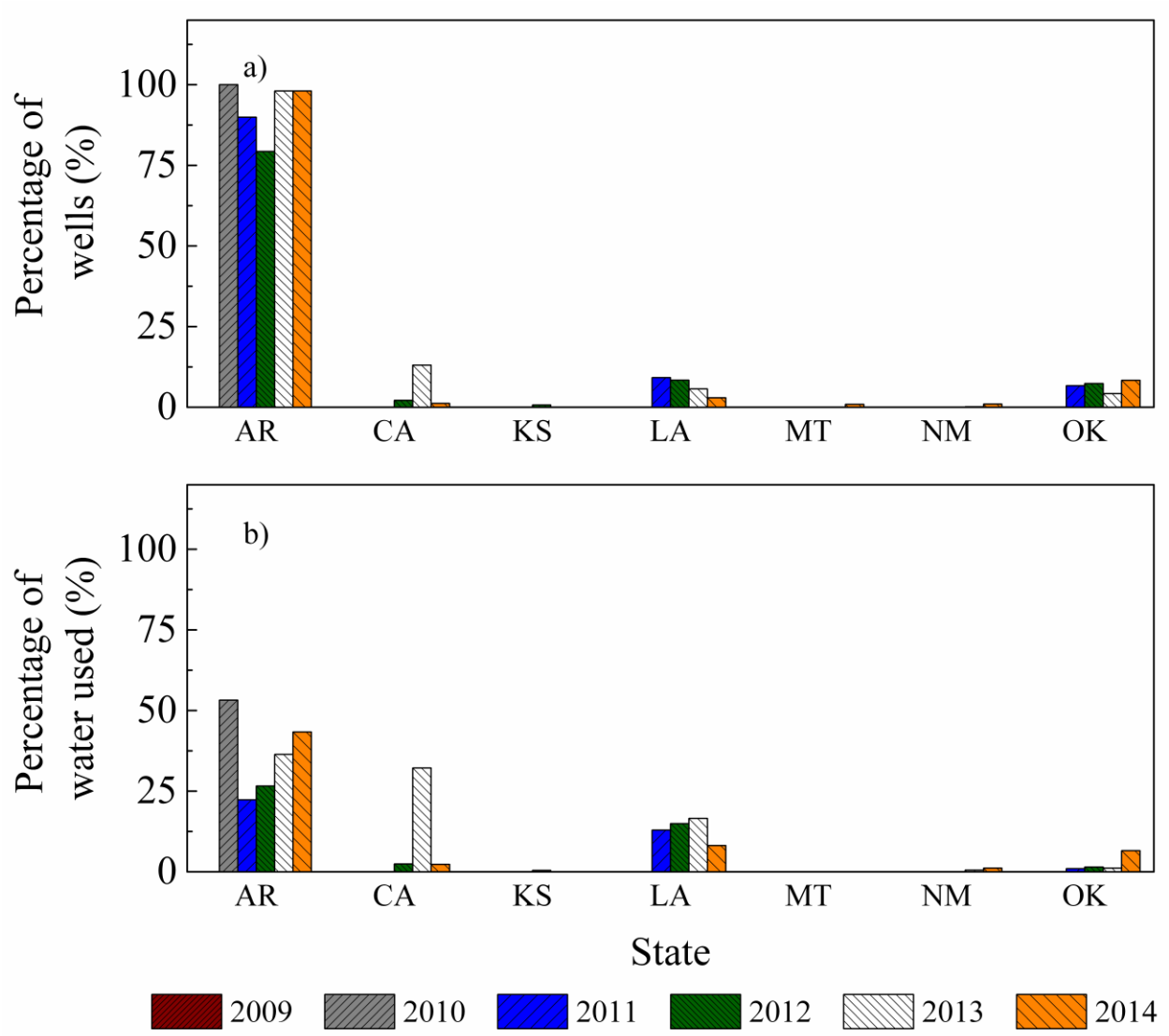

Figure A-11. Recycled water used in hydraulic fracturing for wells each states. a) Percentage of wells using recycled water with respect to the total wells completed in each state; b) Percentage of water volume being recycled with respect to the total water used during well completion.

Appendix B

Equation A-1

Growth rate in number of wells

$$r_i = \frac{n_{i+1} - n_i}{d_{i+1} - d_i}$$

r_i, the growth rate in i fracturing date;
n_i, the number of wells in i fracturing date;
d_{i+1} - d_i, the interval between i and i+1 fracturing date, days.

Table A-12. Wells fractured with two times.

State	County	API Number	Well Name and Number	Longitude	Latitude
Pennsylvania	Bradford	37-015-20573-00	morgan (01-074-01)	76.85991111	41.76940833
Pennsylvania	Bradford	37-015-20574-00	morgan (01-074-02)	76.85981944	41.76941389
Pennsylvania	Bradford	37-015-20575-00	morgan (01-074-03)	76.85972778	41.76941944
Pennsylvania	Bradford	37-015-20907-00	roy (03-040-01)	76.85587778	41.90235833
Pennsylvania	Bradford	37-015-20908-00	roy (03-040-02)	76.85579167	41.90238611
Pennsylvania	Bradford	37-015-21344	pmg god unit 1h	-76.341069	41.715303
Pennsylvania	Greene	37-059-25323	nv-26cv	-80.28084	39.9864
Pennsylvania	Indiana	37-063-37135	hcpp a 3h	-79.198078	40.524617
Pennsylvania	Jefferson	37-065-26919-00-00	bowers 1a	-78.857475	40.955597
Pennsylvania	Sullivan	37-113-20102	kuziak unit 1h	-76.705917	41.559722
Pennsylvania	Susquehanna	37-115-20427	squier unit 1h	-75.855472	41.671611
Pennsylvania	Susquehanna	37-115-20492	hess, r. 2h	-75.868883	41.759547
Pennsylvania	Susquehanna	37-115-20494	hess, r. 3h	-75.86885	41.759517
Pennsylvania	Susquehanna	37-115-20637	corbin, j. 1h	-75.809614	41.739883
Pennsylvania	Susquehanna	37-115-20639	corbin, j. 3h	-75.809614	41.739969
Pennsylvania	Susquehanna	37-115-20640	corbin, j. 4h	-75.809614	41.740006
Pennsylvania	Susquehanna	37-115-20728	hess, r. 5h	-75.868814	41.759483
Pennsylvania	Susquehanna	37-115-20935	bunnell, e. 5h	-75.847153	41.780744
Pennsylvania	Susquehanna	37-115-20936	bunnell, e. 6h	-75.847158	41.780661
Pennsylvania	Susquehanna	37-115-20937	bunnell, e. 10h	-75.847156	41.780703
Pennsylvania	Susquehanna	37-115-21023-00-00	aldrich, l. 5h	-75.599947	41.785272
Pennsylvania	Westmoreland	37-129-28482	cook unit 16h	-79.681833	40.243833
Pennsylvania	Westmoreland	37-129-28483	cook unit 17h	-79.681806	40.243778

Table A-13. Inorganic Compounds.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
hydrogen chloride	7647-01-0	5008	6094	5	4973	1513.0	5.26-430000
crytalline silica	14808-60-7	4358	6416	1	4330	115776.6	5.20-892950
ammonium chloride	12125-02-9	1667	1821	7	1655	858045.8	0.06-2000000
sodium chloride	7647-14-5	1078	1104	126	841	41.0	0.20-10495
sodium persulfate	7775-27-1	786	791	82	684	355523.8	107.20-1000000
sodium hydroxide	1310-73-2	782	898	13	731	82.0	0.04-14993
ammonium persulfate	7727-54-0	727	761	23	703	9.7	0.10-3357
ammonium sulfate	7783-20-2	528	535	0	361	59.5	0.10-959
sodium sulfate	7757-82-6	414	415	53	357	30.7	0.10-1545
potassium carbonate	584-08-7	412	425	29	381	270.5	0.70-24650
calcium chloride	10043-52-4	333	340	0	320	14.9	0.10-86
potassium chloride	7447-40-7	217	231	1	212	56.6	0.20-473
various chlorides	16887-00-6	196	200	79	116	50.2	0.80-1900
sodium chlorite	7758-19-2	195	196	0	195	2.8	0.07-112
illite	12173-60-3	191	191	0	191	391.9	5.00-914
biotite	1302-27-8	190	190	0	190	34.3	1.00-80
goethite	1310-14-1	190	190	0	190	91.6	22.00-202
calcite	471-34-1	190	190	0	190	42.2	18.00-78
apatite	64476-38-6	190	190	0	190	58.5	24.60-93
ilmenite	98072-94-7	190	190	0	190	170.8	44.40-348
sodium nitrate	7631-99-4	181	181	0	181	42.2	18.00-78
aluminum oxide	1344-28-1	176	382	1	174	34.0	8.00-75
iron oxide	1309-37-1	174	380	1	172	709.7	11.30-9660
titanium oxide	13463-67-7	174	379	1	172	1468.6	13.60-9832
non-crystalline silica	7631-86-9	152	154	4	147	180.8	1.30-2871
sulfur dioxide	7446-09-5	150	150	138	12	155.9	1.30-1436
sulfuric acid	7664-93-9	150	150	147	3	92.8	0.10-15664
potassium hydroxide	1310-58-3	135	144	6	129	0.1	0.10-0.20
sodium bromide	7647-15-6	132	132	0	131	0.1	0.10-0.10
trisodium ortho phosphate	7601-54-9	122	122	0	122	44.7	0.10-828
sodium carbonate	497-19-8	116	117	0	116	29.7	0.18-1990
sodium perborate tetrahydrate	10486-00-7	81	81	38	43	9.4	2.00-210
boric acid	10043-35-3	77	77	5	72	389.4	0.30-1917
hydrogen peroxide	7722-84-1	77	77	0	77	32.5	0.40-605
chlorine dioxide	10049-04-4	76	76	5	70	10.7	0.14-129
phosphonic acid	13598-36-2	72	75	63	9	27.2	0.70-137
sodium calcium borate	1319-33-1	59	59	59	0	20.8	0.10-120
nitrogen	7727-37-9	56	56	0	54	3.1	0.20-10
phosphoric acid	7664-38-2	51	51	0	44	N/A	N/A
clay	1302-78-9	50	50	7	28	215006.6	757.80-486703
silica gel	112926-00-8	47	47	8	35	13.1	0.09-18
ammonium bisulfite	10192-30-0	34	36	0	34	25.1	0.10-63
potassium borate	1332-77-0	33	33	0	33	0.8	0.10-3
thiocyanic acid, ammonium salt	1762-95-4	32	32	0	32	149.2	1.00-940
magnesium silicate hydrate (talc)	14807-96-6	23	23	0	17	64.3	0.40-366
sodium hypochlorite	7681-52-9	20	20	0	20	4.0	0.10-10
sodium metaborate tetrahydrate	10555-76-7	18	19	3	15	0.1	0.10-0.40
sodium sulfocyanate	540-72-7	14	14	0	14	8.7	3.80-17
strontium chloride	10476-85-4	13	13	1	12	11.9	0.70-93
sodium thiosulfate	7772-98-7	13	13	0	13	1.3	0.10-4
boric acid	1303-86-2	12	12	0	11	6.6	0.20-53
inorganic phosphate	7632-05-5	11	11	0	0	99.4	81.50-123
sodium bisulfite	7631-90-5	9	9	0	9	5.6	0.70-17
copper(ii) sulfate	7758-98-7	9	9	0	4	N/A	N/A
sodium borate decahydrate	1303-96-4	8	8	0	8	3.8	0.50-8
deuterium oxide	7789-20-0	8	8	0	8	5.3	0.10-7
deta-phosphonate	15827-60-8	5	5	0	5	120.7	16.40-317
mullite	1302-93-8	4	6	0	3	104.7	32.60-132
magnesium chloride	7786-30-3	4	4	0	3	156.2	135.30-170
ammonium	8013-59-0	4	4	0	4	32384.3	17531.20-38041
diatomaceous earth, calcined	91053-39-3	4	9	0	4	451.6	451.60-452
potassium metaborate	13709-94-9	3	3	0	3	15.8	6.90-23
silica crystalline-cristobalite	14464-46-1	3	5	0	3	182.2	116.50-249
sulfamic acid	5329-14-6	3	5	0	3	18.7	2.80-63
sodium perborate	7632-04-4	3	3	0	3	6299.5	2504.50-8951
aluminum silicate	1302-76-7	2	2	0	2	13.8	0.35-14

Table A-13. Inorganic Compounds. (Continued)

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
orthoboric acid, potassium salt	20786-60-1	2	2	2	0	N/A	N/A
sodium metabisulfite	7681-57-4	2	4	0	2	0.1	0.09-0.17
sodium perborate monohydrate	10332-33-9	1	1	0	0	N/A	N/A
attapulgite	12174-11-7	1	1	0	1	8.0	8.00-8.00
sodium tetraborate pentahydrate	12179-04-3	1	1	0	1	290.0	290.00-290
CO_2	124-38-9	1	1	0	0	N/A	N/A
calcium oxide (CaO)	1305-78-8	1	1	0	0	N/A	N/A
calcium peroxide	1305-79-9	1	1	0	1	0.7	0.70-1
sodium tetraborate	1330-43-4	1	1	0	1	10.0	10.00-10.00
boric acid,sodium salt	1333-73-9	1	1	0	1	63.8	63.80-64
cupric chloride	7447-39-4	1	1	0	0	N/A	N/A
potassium persulfate	7727-21-1	1	1	1	0	N/A	N/A
sodium metaborate	7775-19-1	1	1	0	0	N/A	N/A
ferrous-sulfate heptahydra	7782-63-0	1	1	0	1	19.1	19.10-19.10
inorganic chemical	N/A	196	200	79	116	261.2	3.30-610
salt	N/A	154	154	0	152	36.4	1.20-52
inorganic salts	N/A	87	147	45	42	180.3	1.70-591
organophilic clay	N/A	36	36	0	36	1.8	0.30-4
inorganic phosphate	N/A	27	27	0	27	7.2	5.50-19
sodium salt	N/A	18	18	0	18	0.7	0.30-1
clay	N/A	10	10	1	9	736.3	0.20-2161
silica	N/A	6	6	0	1	1993.9	1993.90-1994
calcium magnesium sodium phospate frit	N/A	3	3	0	3	1405.3	1405.30-1405.30
amps brine dispersion	N/A	2	2	0	2	1028.3	985.80-1090
alkaline bromide salts	N/A	1	1	0	1	15.3	15.27-15.27
borate suspension	N/A	1	2	0	1	127.2	127.20-127.20
clay stabilizer additive (kcls-4)	N/A	1	1	0	1	5.4	5.40-5.40
hydrated clay	N/A	1	1	0	0	N/A	N/A
inorganic acid	N/A	1	1	0	0	N/A	N/A
inorganic base	N/A	1	1	0	0	N/A	N/A

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

Table A-14. Unknown Compounds.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
citrus terpenes	94266-47-4	79	79	0	78	204.0	1.70-2000
coconut oil (ventura)	8001-31-8	2	2	0	2	0.2	0.18-0.34
not hazardous	N/A	898	1760	263	582	2387.7	0.10-25567
N/A	N/A	510	1369	93	395	834	0.02-77454
surfactants	N/A	470	532	61	310	150.3	0.10-2161
haloalkyl heteropolycycle salt	N/A	152	152	0	152	13.1	0.10-328
unsulphonated matter	N/A	150	150	138	12	0.1	0.10-0.20
mx588-2	N/A	110	110	0	110	153.1	20.00-219
resin based nonionic inhibitor	N/A	95	95	7	88	1.9	0.01-9
friction reducer additive	N/A	90	94	0	53	724.4	381.40-1450
microparticle	N/A	82	82	0	82	15.9	5.06-124
silica substrate	N/A	80	80	0	80	102536.6	73305.80-153268
neutralized organic acid	N/A	78	78	7	71	26.4	3.80-46
component	N/A	76	79	0	75	3.8	0.10-20
soap	N/A	70	70	1	69	712.2	590.40-757
blend	N/A	59	59	52	7	213.8	41.20-471
trade secret	N/A	59	70	0	9	2675.6	93.70-289352
corrosion inhibitor additive (ci-150)	N/A	58	58	0	36	4.6	0.20-10
ingredients	N/A	56	285	7	45	2.2	0.01-9
blend surfactants	N/A	51	51	2	41	8.5	0.60-340
breaker component	N/A	50	56	0	46	15.3	0.10-395
solvent	N/A	49	49	0	43	1095.5	0.10-1994
ammonium salts	N/A	46	46	0	45	4888.0	1.30-26481
whole product	N/A	43	195	0	0	N/A	N/A
other	N/A	40	138	0	40	2008.9	70.00-40432
organic acid derivatives	N/A	39	39	0	28	21.3	16.60-56
demulsifier base	N/A	38	38	0	22	6.2	1.43-25
bacteria culture	N/A	30	30	0	30	97.3	26.90-127
mc mx 8-2544	N/A	25	25	0	25	88.5	10.00-151
none	N/A	25	25	25	0	N/A	N/A
essential oils	N/A	21	21	0	20	1389.88.3	916.20-16760.20-12
alkali chloride salt	N/A	16	16	1	15	N/A	N/A
non-msds	N/A	16	24	0	0	134.4	72.20-153
scale inhibitor	N/A	14	14	0	14	370.811.3	180.00-4700.40-51
fr-200w	N/A	12	12	0	12	75.9	1.50-336
inerts	N/A	11	11	0	11	N/A	N/A
cured acrylic resin	N/A	7	7	0	7	N/A	N/A
hemicellulase breaker	N/A	7	7	0	0	18.5	18.50-19
nickel chelate catalyst	N/A	7	8	0	0	N/A	N/A
acid	N/A	6	6	0	1	18.5	18.50-19
aqueous solution	N/A	6	6	0	0	1993.9	1993.90-1994
biocide	N/A	6	6	0	1	0.6	0.20-1
disinfectant	N/A	6	6	0	1	1993.9	1993.90-1994
pine oil	N/A	6	6	0	6	2.7	0.30-5
weak acid	N/A	6	6	0	1	3430.6	88.23-13193
buffer	N/A	3	3	0	3	N/A	N/A
walnut hulls	N/A	3	3	0	3	N/A	N/A
3rd party proprietary	N/A	2	2	0	0	6.6	6.60-7
borate salts	N/A	2	2	0	0	42.2	40.20-46
feriplex 40 - other (57-58.5)	N/A	2	2	0	2	2628.6	2567.60-2683
iron control additive (fe-200l)	N/A	2	2	0	2	170.3	164.10-177
patented synthetic acid	N/A	2	2	0	2	2.9	2.90-3
phosphonic acid ammonium salt	N/A	2	2	0	2	1.6	1.60-2
plexbreak 145 - other (85)	N/A	2	2	0	2	N/A	N/A
plexhib 256 - other (52-66)	N/A	2	2	0	2	1244.9	1244.90-1245
undisclosed by supplier	N/A	2	2	0	0	20.6	20.60-21
*supplied by operator	N/A	1	1	0	1	17.7	17.70-18
greenskeeper solvent	N/A	1	1	0	1	1.9	1.90-2
lca-1	N/A	1	1	0	1	N/A	N/A
not listed	N/A	1	1	0	1	1095.5	1095.50-1096
organic salt	N/A	1	26	1	0	0.6	0.60-1
quaternary salt	N/A	1	1	0	1	204.0	1.70-2000
suspension add	N/A	1	1	0	1	0.2	0.18-0.34

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

Table A-15. Organics with Frequency smaller than 25.

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
Alkoxy							
oxyakylated amine quat	138879-94-4	7	7	1	6	3.7	3.55-4
oxyalkylated polymer	N/A	24	24	0	24	17.8	0.70-26
aliphatic alcohol glycol ether	N/A	6	6	0	6	12.8	0.20-17
oxyalkylated alkylphenols	N/A	1	2	1	0	N/A	N/A
oxyalkylated amine	N/A	1	1	1	0	N/A	N/A
Ethoxy							
tridecyl alcohol, ethoxylated	24938-91-8	22	22	8	9	0.7	0.10-2
alcohols, c6-12, ethoxylated	68439-45-2	11	11	0	11	270.7	0.79-444
ethylene oxide	75-21-8	11	11	0	11	0.2	0.10-0.30
coco amine	61791-14-8	8	8	0	8	0.6	0.20-2
polyethylene-polypropylene glycol	9003-11-6	8	8	0	8	272.8	154.20-444
poly(oxyethylene) sorbitol monostearate	9005-67-8	8	8	0	8	5.1	0.40-9
ethoxylated octylphenol	9036-19-5	7	7	0	7	37.4	32.10-44
alcohols, C12-18, ethoxylated propoxylated	69227-21-0	6	6	0	6	22.7	14.30-27
oxirane, methyl-, polymer with oxirane, mono(2-ethylhexyl) ether	64366-70-7	5	5	0	5	80.4	0.80-115
alcohols, c10-12, ethoxylated	67254-71-1	4	4	0	2	0.2	0.20-0.20
polyethylene glycol (5) undecyl ether	34398-01-1	3	4	1	2	86.9	86.70-87
polyethylene glycol trimethylnonyl ether	60828-78-6	2	2	0	2	1.2	0.88-2
formaldehyde polymer with methyl oxirane, 4-nonylphenol and oxirane	63428-92-2	2	2	0	2	9.7	6.90-12
ammonium c6-10-alkyl polyoxyethylene sulfate	68037-05-8	2	2	0	2	1.5	1.14-2
poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy-, mono-c8-10-alkyl ethers, phosphates	68130-47-2	2	2	0	2	0.2	0.18-0.34
amines, polyethylenepoly-, ethoxylated, phosphonomethylated	68966-36-9	2	2	0	2	81.9	33.00-115
dipropylene glycol monomethyl ether	34590-94-8	1	1	0	1	0.2	0.20-0.20
amines, tallow alkyl, ethoxylated	61791-26-2	1	1	0	1	0.6	0.60-1
alcohols, c12-13, ethoxylated	66455-14-9	1	1	0	1	4.0	4.00-4.00
alcohols, c9-11, ethoxylated	68439-46-3	1	1	0	1	19.0	19.00-19.00
glycol ethers	9004-77-7	1	1	0	1	8.1	8.10-8.10
Carbohydrates & Enzyme							
xanthan gum	11138-66-2	2	2	0	2	121.6	0.20-441
hydroxypropyl guar gum	39421-75-5	2	2	0	2	4.8	3.00-7
Carboxylic Acids & their Salts							
sodium glycolate	2836-32-0	21	21	0	1	92.7	92.70-93
glycolic acid	79-14-1	19	19	0	19	12.3	0.10-2762
gluconic acid	526-95-4	17	17	0	17	21.1	3.20-100
peracetic acid	79-21-0	12	12	0	12	77.3	69.10-85
erythorbic acid	89-65-6	1	1	0	0	N/A	N/A
aliphatic acid, potassium salt		3	3	0	3	0.2	0.20-0.20
Alcohols							
heptene, hydroformylation products, high-boiling	68526-88-5	9	9	0	9	4.5	1.30-15
butan-1-ol	71-36-3	7	7	0	7	30.7	1.50-63
secondary alcohol	N/A	21	21	0	21	1336.1	14.50-1676
acetylenic alcohols	N/A	6	6	0	6	0.6	0.20-1
organic alcohol	N/A	5	5	0	5	221.2	3.30-895
glycol	N/A	4	4	0	3	131.9	67.40-180
alkyl alcohol	N/A	3	3	0	3	190.3	186.80-193
hydroxylated hydrocarbon	N/A	1	1	0	0	N/A	N/A
Aldehydes							
acetaldehyde	75-07-0	11	11	0	11	16.8	0.10-263
Others in Organics containing O							
methyl borate	121-43-7	10	10	0	10	4.3	0.20-12
epichlorohydrin	106-89-8	2	4	0	2	0.1	0.09-0.17
alcohol derivative	N/A	11	11	0	11	15.6	5.00-41
silicane derivative	N/A	4	4	0	4	0.2	0.10-1
dimethyl siloxanes and silicones	N/A	3	3	0	3	0.1	0.10-0.10
Polymers							
poly(tetrafluoroethylene)	9002-84-0	8	8	0	2	0.1	0.10-0.10
poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, mono-C10-14-alkyl ethers, phosphates	68585-36-4	6	6	0	6	22.7	14.30-27
polyethylene glycol oleate ester	56449-46-8	5	6	0	3	0.2	0.20-0.20

Table A-15. Organics with Frequency smaller than 25. (Continued)

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
alkenes, c24-25 α-, polymers with maleic anhydride, docosyl esters	68607-07-8	3	4	0	3	40.4	27.70-59
formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane	29316-47-0	2	2	0	2	4.8	3.40-6
gelatin	9000-70-8	2	2	0	2	1.4	0.60-3
styrene acrylic copolymer	25085-34-1	1	1	0	0	N/A	N/A
2-propen-1aminium, n,n- dimethyl-n-2-propenyl-,chloride, homopolymer	26062-79-3	1	1	0	1	38.4	38.40-38.40
anionic water soluble polymer	N/A	21	21	0	20	292.3	9.70-2240
acrylamide modified polymer	N/A	20	20	0	19	883.2	71.30-987
polyacrylamide powder and other	N/A	14	14	0	14	461.4	370.00-588
aliphatic polyol	N/A	13	13	0	13	161.9	14.90-431
copolymer	N/A	7	7	0	2	7.1	0.10-19
vinyl copolymer	N/A	6	6	0	6	597.6	137.30-781
polycarboxylate	N/A	5	5	0	5	51.2	5.90-112
non-hazardous polymers	N/A	4	4	0	4	55.1	20.90-76
synthetic organic polymer	N/A	4	4	0	4	1756.7	588.60-6078
acrylamide, 2-acrylamido-2 methylpropanesulfonic acid, sodium salt polymer	N/A	3	3	0	3	160.2	160.20-160.20
aliphatic co-polymer	N/A	3	3	0	3	18.5	18.20-19
aliphatic polyglycol ether	N/A	3	3	0	3	2.8	2.80-3
ethylene-vinyl acetate copolymer	N/A	3	4	0	3	6.7	4.60-10
polycarboxylic acid polymer	N/A	3	3	0	3	217.9	190.70-233
polyether	N/A	3	3	0	3	0.2	0.20-0.20
polyglycol ester	N/A	3	3	0	3	18.0	4.40-25
sulfonated polystyrene	N/A	3	3	0	3	3.5	2.80-4
thiourea copolymer	N/A	3	3	0	3	2.8	2.80-3
anionic polyacrylamide polymer	N/A	2	2	0	2	8.2	5.60-12
resin	N/A	2	2	0	2	4456.9	4430.20-4484
copolymer resin	N/A	1	1	0	1	5379.5	5379.50-5380
polyactide resin	N/A	1	1	0	1	100.0	100.00-100.00
water-soluble polymer	N/A	1	1	0	1	1415.3	1415.30-1415.30
Naphtha							
hydrotreated light distillate	54742-47-8	11	11	0	11	1018.7	480.00-5200
napthenic oil	64742-52-5	4	4	1	3	98.3	0.10-210
mineral oil	8042-47-5	3	4	0	3	6.7	4.60-10
solvent naptha (petroleum), medium aliphatic	64742-88-7	2	2	0	2	0.1	0.09-0.17
hydrotreated light distillate		1	1	0	1	133.4	133.40-133.40
Alkanes							
c-11 to c-14 n-alkanes, mixed	1120-21-4, 112-40-3, 629-50-5, 629-59-4	9	9	0	9	380.3	238.20-499
c-12 n-alkanes	1120-40-3	3	4	0	3	12.7	6.90-23
iso-alkanes/n-alkanes	N/A	3	3	0	3	116.0	1.60-281
modified alkane	N/A	1	1	0	1	50.7	50.70-51
Alkenes							
alkenes	N/A	1	1	0	1	0.1	0.10-0.10
Others in hydrocarbons							
d-limonene	8028-48-6	5	5	0	5	27.6	0.30-38
hydrocarbon solvent	N/A	2	2	0	2	19.4	5.10-78
Benzyl							
n-alkyl dimethyl benzyl ammonium chloride (c12-18)	68391-01-5	23	23	0	23	71.2	16.80-199
cyclohexene	5989-27-5	21	22	1	19	123.3	0.80-322
n-alkyl dimethyl ethylbenzyl ammonium chloride (c12-14)	85409-23-0	19	19	0	19	33.2	16.80-38
alkyl dimethyl benzyl ammonium chloride	139-08-2	16	16	0	16	6.9	5.20-9
polyethlenepolyamine	68603-67-8	8	8	0	8	1.1	0.40-3
phenol formaldehyde resin	9003-35-4	6	6	0	6	15603.7	99.10-140084
dodecylbenzenesulfonate isopropanolamine	42504-46-1	5	5	0	4	8.1	0.62-9
pyridine, alkyl derives., quaternized with benzyl chloride	68909-18-2	5	5	0	5	1.9	1.70-2
n-alkyl-n-benzylpyridinium chloride	100765-57-9	4	4	0	4	18.7	15.00-27
isomeric aromatic ammonium salt	35674-56-7	1	1	0	1	24.2	24.20-24.20

Table A-15. Organics with Frequency smaller than 25. (Continued)

Ingredients	CAS no.	Num. of Wells	Freq. [a]	Mean conc., ppm [d]			
				N [b]	N [c]	mean	range
alkaryl compound	N/A	1	1	0	0	N/A	N/A
Phenyl							
direct red 81	2610-11-9	7	7	0	0	N/A	N/A
methyl salicylate	119-36-8	2	2	0	0	N/A	N/A
benzoic acid	65-85-0	1	1	0	1	36.6	36.60-37
aromatic hydrocarbon	N/A	17	17	0	17	0.8	0.10-2
aromatic ketones	N/A	11	11	0	11	10.1	1.20-15
isomeric aromatic ammonium	N/A	7	7	0	7	1.0	0.10-10
Nitrogen							
triethanolamine hydroxyacetate	68299-02-5	19	19	0	19	58.3	0.80-11048
triethanoiamine	102-71-6	14	14	0	14	14.1	3.10-67
erucic amidopropyl dimethyl betaine	149879-98-1	14	14	0	14	331.6	24.20-707
tall oil acid diethanolamide	68155-20-4	13	14	0	7	241.6	42.60-921
monethanolamine boate	26038-87-9	11	11	0	10	6061.0	7.00-107157
ethylenediaminetetraacetic acid	60-00-4	11	11	0	11	16.7	0.30-34
acrylonitrile	107-13-1	9	9	2	7	0.4	0.30-1
tetramethylammonium chloride	75-57-0	9	9	0	9	135.4	6.60-500
monoethanolamine hydrochloride	2002-24-6	8	8	0	8	36.4	24.20-43
organophilic clay	68953-58-2, 68911-87-5, 14808-60-7	7	7	0	7	34.8	27.50-61
formamide	75-12-7	6	6	0	6	3.8	1.30-5
ethanol, 2,2',2"-nitrilotris-, 1,1',1"-tris(dihydrogen phosphate), sodium salt	68171-29-9	5	5	0	5	32.8	27.50-52
boric acid (2-aminoethanol)	68425-67-2	5	5	0	4	69.8	0.70-180
sulfamic acid, n-bromo, sodium salt	1004542-84-0	4	4	0	4	13.8	12.60-16
n,n-dimethyl-1,3-propanediamine	109-55-7	2	2	0	2	0.1	0.09-0.17
n-dodecyl-2-pyrrolidone	2687-96-9	2	2	0	2	467.9	50.00-3788
cocamidopropyl dimethylamine	68140-01-2	2	2	0	2	0.2	0.18-0.34
organic phosphonate	70714-66-8	2	2	0	0	N/A	N/A
2-aminoethanol	9007-33-4	2	2	0	0	N/A	N/A
fatty acid amidoalkyl betaine	N/A	9	9	0	9	355.1	0.70-830
alkyl amine surfactant	N/A	3	3	0	3	0.8	0.80-1
fatty amino adduct	N/A	3	3	0	3	5.8	5.70-6
cocoamido tertiary amine	N/A	2	2	0	0	N/A	N/A
inner salt of alkylamines	N/A	2	2	0	2	2939	2939.00-2939.00
amine triphosphate	N/A	1	1	0	1	15.8	15.80-16
organic amine resin	N/A	1	1	0	1	15.3	15.30-15.30
Sulfur							
sulfonic acids, c-14-16- alkane hydroxy and c14-16-alkene, sodium salts	68439-57-6	1	1	0	1	119.2	119.20-119.20
sulfonated hydrocarbon	N/A	1	1	0	0	N/A	N/A
Phosphorous							
phosphonic acid ester	N/A	12	12	0	12	3.0	2.60-3
organic phosphonic acid salts	N/A	4	5	0	4	109.5	14.80-514
alkyl phosphate ester	N/A	2	2	0	0	N/A	N/A

[a] Frequency; [b] Num. of wells with conc. of 0; [c] Num. of wells with conc. larger than 0; [d] Mean concentration in hydraulic fracturing fluids, ppm; N/A: not available.

Table A-16. Num. of wells recycling produced water

Operators	Num. of wells		Percentage
	Recycled [a]	Recycled [a]	%
Chesapeake Appalachia	433	494	87.7
Chesapeake Operating, Inc.	176	198	88.9
Talisman Energy USA	146	253	57.7
Swepi LP	139	228	61.0
Southwestern Energy	119	220	54.1
Energy Corporation of America	80	80	100.0
Shell Oil Company Affiliate	14	70	20.0
Edgemarc Energy Holdings, LLC	2	2	100.0
EXCO Resources	2	84	2.4
Cabot Oil & Gas Corporation	1	290	0.3
Total	1,112	1,919	57.9

[a] num. of wells which recycled produced water.
[b] num. of wells owned by certain operator.

Appendix C

Equation A-2

Volume of chemical additives

$$V_{ca} = V_{TWV} \times \frac{PR_t - PR_w - PR_p}{PR_w}$$

V_{ca} volume of chemical additives used to fracturing a well, gal;
V_{TWV}, total water volume used in fracturing a well, gal
PR_p, percentage of proppants in hydraulic fracturing fluids, % by mass; (Note: observations with the CAS No. of 7631-86-9, 1302-78-9, 1302-93-8, 1302-27-8, 14808-60-7, or 14464-46-1 were considered as the proppants.)
PR_w, percentage of water in hydraulic fracturing fluids in reports, % by mass;
PR_t, total percentage of all the ingredients in hydraulic fracturing fluids in reports, % by mass.

Equation A-3

Chemical concentrations in chemical additives

$$C_{i,ca} = C_{i,HFFs} \times \frac{PR_t}{PR_t - PR_w - PR_p}$$

$C_{i,\ ca}$, chemical *i*'s concentration in chemical additives, ppm;
$C_{i,\ HFFs}$, chemical *i*'s concentration hydraulic fracturing fluids, ppm;
PR_p, percentage of proppants in hydraulic fracturing fluids, % by mass; (Note: observations with the CAS No. of 7631-86-9, 1302-78-9, 1302-93-8, 1302-27-8, 14808-60-7, or 14464-46-1 were considered as the proppants.)
PR_w, percentage of water in hydraulic fracturing fluids in reports, % by mass;
PR_t, total percentage of all the ingredients in hydraulic fracturing fluids in reports, % by mass.

Equation A-4

Weighted fracturing days based on the wells

$$t_{wfd} = \frac{\sum_{=1}^{j=14}(n_j \times j)}{\sum_{j=1}^{j=14} n_j}$$

j, fracturing days, days;
n_j, number of wells which were fractured by j days;
t_{wfd}, weighed fracturing days, days.

Equation A-5

Normalized water percentages in hydraulic fracturing fluids

$$PR_{nw} = \frac{PR_w}{PR_t} \times 100\%$$

PR_{nw}, normalized percentage of water in hydraulic fracturing fluids, % by mass;
PR_w, percentage of water in hydraulic fracturing fluids in reports, % by mass;
PR_t, total percentage of all the ingredients in hydraulic fracturing fluids in reports, % by mass.

Equation A-6

Antoine equation (Mackay and Boethling, 2000)

$$\log_{10} P = A + B \times \left(\frac{1}{T + 18 - 0.19 \times T_b} - \frac{1}{0.81 \times T_b + 18}\right)$$

T, temperature inputted into MPBPWIN ™, K;
T_b, boiling points obtained from MPBPWIN ™, K;
P, pure vapor pressure at temperature T obtained from MPBPWIN ™, atm;
A, B, component-specific constants.

Equation A-7

Grain-Watson equation (Mackay and Boethling, 2000)

For liquids,

$$\log_{10} P = A + B \times \left[1 - \frac{\left(3 - 2 \times \frac{T}{T_b}\right)^{\left(0.4133 - 0.2575 \times \frac{T}{T_b}\right)}}{T/T_b} - 2 \times \left(0.4133 - 0.2575 \times \frac{T}{T_b}\right) \times \left(3 - 2 \times \frac{T}{T_b}\right)^{\left(-0.5867 - 0.2575 \times \frac{T}{T_b}\right)} \times \ln \frac{T}{T_b}\right]$$

For solids,

$$\log_{10} P = A + B \times \left[1 - \frac{\left(3 - 2 \times \frac{T}{T_b}\right)^{\left(0.4133 - 0.2575 \times \frac{T}{T_b}\right)}}{T/T_b} - 2 \times \left(0.4133 - 0.2575 \times \frac{T}{T_b}\right) \times \left(3 - 2 \times \frac{T}{T_b}\right)^{\left(-0.5867 - 0.2575 \times \frac{T}{T_b}\right)} \times \ln \frac{T}{T_b}\right]$$

$$+ 0.6 \times \ln(R \times T_m) \times \left[1 - \frac{\left(3 - 2 \times \frac{T}{T_m}\right)^{\left(0.4133 - 0.2575 \times \frac{T}{T_m}\right)}}{T/T_m} - 2 \times \left(0.4133 - 0.2575 \times \frac{T}{T_m}\right) \times \left(3 - 2 \times \frac{T}{T_m}\right)^{\left(-0.5867 - 0.2575 \times \frac{T}{T_m}\right)} \times \ln \frac{T}{T_m}\right]$$

T, temperature inputted into MPBPWIN ™, K;
T_b, the boiling point obtained from MPBPWIN ™, K;
T_m, the melting point obtained from MPBPWIN ™, K;
P, pure vapor pressure at temperature T obtained from MPBPWIN ™, atm;
A, B, component-specific constants.

Equation A-8

Volume of chemical additives stored daily

$$V_{j,S} = V_{ca} \times \frac{t_{fd} - j + 1}{t_{fd}}$$

$V_{j,S}$, storage volume of chemical additives at j^{th} day, gal;
V_{ca}, volume of chemical additives used to fracture a well, gal;
t_{fd}, days used for hydraulic fracturing, days.

Equation A-9

Daily consumption volume of chemical additives

$$V_{j,W} = \frac{V_{ca}}{t_{fd}}$$

$V_{j,W}$, consumption volume of chemical additives at j^{th} day, gal;
V_{ca}, volume of chemical additives used to fracture a well, gal;
t_{fd}, days used for hydraulic fracturing, days.

Equation A-10

Standing loss from vertical fixed-roof storage tanks

$$L_{j,S} = \frac{L \times W \times (H_S - H_L) \times \sum_i \left(M_i \times \frac{P_i}{\sum_i P_i}\right) \times \sum_i P_i \times 0.0018 \times (0.72 \times (T_{AX} - T_{AN}) + 0.028 \times a \times I) \times n}{R \times (0.44 \times (T_{AX} + T_{AN})/2 + 0.56 \times ((T_{AX} + T_{AN})/2 + 6 \times a - 1) + 0.0079 \times a \times I) \times (1 + 0.053 \times \sum_i P_i \times (H_S - H_L))}$$

$$L_S = \sum_j L_{j,S}$$

n, number of chemical storage tanks, unitless;
$L_{j,S}$, standing loss at j^{th} day, lb day^{-1}.
L_s, standing loss, lb well^{-1}.

Equation A-11

Working losses from vertical fixed-roof storage tanks

$$L_{j,W} = 0.0010 \times \sum_i \left(M_i \times \frac{P_i}{\sum_i P_i}\right) \times \sum_i P_i \times K_N \times K_P \times V_{j,W} \times 0.178107607$$

$$L_W = \sum_j L_{j,W}$$

$V_{j,W}$, consumption volume of chemical additives at j^{th} day, ft^3;
$L_{j,W}$, working loss at j^{th} day, lb day^{-1}.
L_W, working loss, lb well^{-1}.

Equation A-12

95% Confidence interval

$$\overline{X} \pm Z_{\alpha/2}\left(\frac{\sigma}{\sqrt{n}}\right)$$

$\overline{X}$, the average value;
σ, standard deviation;
α, confidence level, α = 0.05 for 95% confidence interval;
Z, confidence coefficient, $Z_{0.025} = 1.96$;
n, sample size, n=10,000 for 10,000 runs.

Equation A-13

Stagnant two-film model (Bloomdahl et al., 2014)

$$Flux = \left(\frac{1}{(Z_W/D_W) + (Z_a/D_a K_H)}\right)\left(C_w - \frac{C_a}{K_H}\right)$$

Z_a, thickness of air layer, cm;
Z_w, thickness of water layer, cm;
D_a, diffusivity of constituent in air, $cm^2\ s^{-1}$;
D_w, diffusivity of constituent in water, $cm^2\ s^{-1}$;
K_H, Henry's constant, dimensionless;
C_a, air concentration of constituent, $\mu g\ cm^{-3}$;
C_w, water concentration of constituent, $\mu g\ cm^{-3}$;
Flux, $\mu g\ cm^{-2}\ s^{-1}$.

Table A-17. Fracturing days weight to the number of wells.

Fracturing days	Num. of wells	Cumulative Percentages, %	Weighed fracturing days
1	12631	28.32	1.00
2	7151	44.35	1.36
3	4411	54.24	1.66
4	3335	61.71	1.94
5	2833	68.06	2.23
6	2331	73.29	2.50
7	1903	77.56	2.75
8	1546	81.02	2.97
9	1246	83.81	3.17
10	960	85.97	3.34
11	836	87.84	3.51
12	665	89.33	3.65
13	642	90.77	3.80
14	447	91.77	3.91
Total	40,937	NA	NA

NA: not available.

Table A-18. Number of wells used to calculate the organic emission.

State	Num. of wells
AR	2,433
CA	1,869
CO	7,549
KS	439
LA	1,219
MT	421
ND	5,301
NM	2,163
OH	667
OK	6,492
PA	3,668
TX	36,546
WV	602
WY	2,654
Total	72,023

Table A-19. Distance between wells and the nearest solar and meteorological observation stations.

Percentiles (%)	Distance to the nearest solar insolation station		Distance to the nearest meteorological station	
	(km)	(miles)	(km)	(miles)
5	11.02	6.85	5.16	3.21
10	16.34	10.15	7.59	4.72
25	28.36	17.63	12.58	7.82
50	47.48	29.50	19.57	12.16
75	65.55	40.73	27.67	17.20
90	78.64	48.86	35.68	22.17
95	85.63	53.21	39.98	24.84

Note 1: using fracturing days as the observations, instead of the number of wells; Note 2: there were 284,616 observations for 72,023 wells.

Table A-20. Descriptions about the variables in the AP-42 model.

Variables	Units	Descriptions
a	dimensionless	Tank paint solar absorptance
C_i	%	Concentration of component i
L	ft.	Tank length
W	ft.	Tank width
H_L	ft.	Maximum liquid height
H_S	ft.	Tank height
I	btu $(ft^2 \cdot day)^{-1}$	Daily total solar insolation on a horizontal surface
K_E	dimensionless	Vapor space expansion factor
K_N	dimensionless	Turnover factor
K_P	dimensionless	For crude oils, K_P=0.75; for organic liquid, K_P=1
K_S	dimensionless	Vented vapor saturation factor
$L_{j,S}$	lb day^{-1}	Daily standing storage loss
$L_{j,T}$	lb day^{-1}	Daily total loss
$L_{j,Ti}$	lb day^{-1}	Daily emission rate of component i
$L_{j,W}$	lb day^{-1}	Daily working loss
M_i	lb $(lb \cdot mole)^{-1}$	Molecule weight of component i
N	dimensionless	Number of turnovers per year
n	dimensionless	Number of chemical storage tanks
P	psia	Vapor pressure of pure component i at the daily average liquid surface temperature
P_i	psia	Partial pressure of component i
P_{VA}	psia	Vapor pressure at daily average liquid surface temperature
Q	bbl day^{-1}	Net throughput (tank capacity [bbl] times turnover rate)
R	psia ft^3 $(lb\text{-}mole\ °R)^{-1}$	Ideal gas constant
T_{AA}	°R	Daily average ambient temperature
T_{AN}	°R	Daily minimum ambient temperature
T_{AX}	°R	Daily maximum ambient temperature
T_B	°R	Liquid bulk temperature
T_{LA}	°R	Daily average liquid surface temperature
V_{ca}	ft^3	Volume of chemical additives used to fracturing a well
$V_{j,S}$	ft^3	Daily on-site storage volume
$V_{j,W}$	ft^3	Daily consumption volume
V_{LX}	ft^3	Tank maximum liquid volume
V_V	ft^3	Vapor space volume
W_V	lb ft^{-3}	Vapor density
x_i	lb-mole $(lb\text{-}mole)^{-1}$	Mole fraction
y_i	lb-mole $(lb\text{-}mole)^{-1}$	Vapor mole fraction
Z_{Vi}	lb lb	Weight fraction of component i in the vapor

Note: referring from Table 7.1-1 in the manual (U.S. EPA, 2006).

Table A-21. Equations in the AP-42 model for the daily loss from the vertical fixed-roof tanks storing chemical additives (U.S. EPA, 2006).

No.	Equations
Equation A-14	$K_E = 0.0018 \times (0.72 \times (T_{AX} - T_{AN}) + 0.028 \times a \times I)$
Equation A-15	$T_{LA} = 0.44 \times T_{AA} + 0.56 \times T_B + 0.0079 \times a \times I$
Equation A-16	$T_{AA} = \frac{T_{AX} + T_{AN}}{2}$
Equation A-17	$T_B = T_{AA} + 6 \times a - 1$
Equation A-18	$x_i = \frac{C_i/M_i}{\sum(C_i/M_i)}$
Equation A-19	$P_i = P \times x_i$
Equation A-20	$P_{VA} = \sum P_i$
Equation A-21	$y_i = \frac{P_i}{P_{VA}}$
Equation A-22	$M_V = \sum(M_i \times y_i)$
Equation A-23	$W_V = \frac{M_V \times P_{VA}}{R \times T_{LA}}$
Equation A-24	$H_{VO} = H_S - H_L$
Equation A-25	$V_{LX} = L \times W \times H_L$
Equation A-26	$n = V_{ca}/V_{LX}$
Equation A-27	$V_V = L \times W \times (H_S - H_L)$
Equation A-28	$K_S = \frac{1}{1 + 0.053 \times P_{VA} \times H_{VO}}$
Equation A-29	$L_{j,S} = V_V \times W_V \times K_E \times K_S \times n$
Equation A-30	$Q = (V_{w,j}/n) \times 0.178107607$
Equation A-31	$N = 5.614 \times \frac{(Q \times 365)}{V_{LX}}$ For N ≤ 36, $K_N = 1$; For N > 36, $K_N = \frac{(180+N)}{(6\times N)}$
Equation A-32	$L_{j,W} = 0.0010 \times M_V \times P_{VA} \times Q \times K_N \times K_P \times n$
Equation A-33	$L_{j,T} = L_{j,W} + L_{j,S}$
Equation A-34	$Z_{Vi} = \frac{y_i \times M_i}{M_V}$
Equation A-35	$L_{j,Ti} = Z_{Vi} \times L_{j,T}$

Table A-22. Input parameters in the AP-42 model (U.S. EPA, 2006).

Variables	Units	Descriptions
Meteorology		
TAN	°R	Daily minimum ambient temperature
TAX	°R	Daily maximum ambient temperature
I	Btu (ft2 day) -1	Daily total solar insolation on a horizontal surface
Tanks		
a	dimensionless	Tank paint solar absorptance
L	ft.	Tank length
W	ft.	Tank width
HL	ft.	Maximum liquid height
HS	ft.	Tank height
Chemicals		
Pi	psia	Partial pressure of component i
Ci	%	Concentration of component i
Mi	lb (lb-mole)-1	Molecule weight of component i
Vj, S	ft3	Daily on-site storage volume
Vj, W	ft3	Daily consumption volume

Table A-23. Dimensions of Intermediate bulk containers (IBCs).

Brands	Accessed date	Models	Dimensions (L x W x H)		Capacity		H_L/H_S [a]
			inch	m	gal.	m^3	
Uline	2016/5/24	IBC Tank - H-3886	48 x 40 x 46	1.22 x 1.02 x 1.17	275	1.45	0.72
Uline	2016/5/24	IBC Tank - H-4420	48 x 40 x 53	1.22 x 1.02 x 1.35	330	1.67	0.75
Vestil	2016/5/24	IBC-275	48 x 40 x 46.5	1.22 x 1.02 x 1.18	275	1.46	0.71
Vestil	2016/5/24	IBC-330	48 x 40 x 53	1.22 x 1.02 x 1.35	330	1.67	0.75
Hoover container solutions	2016/5/24	NA	48 x 40 x 46	1.22 x 1.02 x 1.17	275	1.45	0.72
Hoover container solutions	2016/5/24	NA	48 x 40 x 54	1.22 x 1.02 x 1.35	330	1.67	0.74

[a] H_L: the maximum liquid height, H_S: the tank height.

Table A-24. Equations from AP-42 Chapter 4.3 for calculating the emissions from the open flowback pits.

Equation No.	Equations
1	For $0 < U_{10} < 3.25$ m s^{-1} and all F/D ratios $k_l(m\,s^{-1}) = (2.78 \times 10^{-6})(D_w/D_{ether})^{2/3}$ For $U_{10} > 3.25$ m s^{-1} and $14 < F/D < 51.2$ $k_l(m\,s^{-1}) = [(2.605 \times 10^{-9})(F/D) + (1.277 \times 10^{-7})](U_{10})^2(D_w/D_{ether})^{2/3}$ For $U_{10} > 3.25$ m s^{-1} and $F/D > 51.2$ $k_l(m\,s^{-1}) = (2.61 \times 10^{-7})(U_{10})^2(D_w/D_{ether})^{2/3}$ For $U_{10} > 3.25$ m s^{-1} and $F/D < 14$ For $U^* < 0.3$ $k_l(m\,s^{-1}) = 1.0 \times 10^{-6} + 144 \times 10^{-4}(U^*)^{2.2}(Sc_L)^{-0.5}$ For $U^* > 0.3$ $k_l(m\,s^{-1}) = 1.0 \times 10^{-6} + 34.1 \times 10^{-4}U^*(Sc_L)^{-0.5}$ Where: $U^*(m\,s^{-1}) = (0.01)(U_{10})\left(6.1 + 0.63(U_{10})\right)^{0.5}$ $Sc_L = \mu_L/(\rho_L D_w)$ $F/D = 2(A/\pi)^{0.5}/D$
2	$k_g(m\,s^{-1}) = (4.82 \times 10^{-3})(U_{10})^{0.78}(Sc_G)^{-0.67}(d_e)^{-0.11}$ Where: $Sc_G = \mu_a/(\rho_a D_a)$ $d_e\,(m) = 2(A/\pi)^{0.5}$
7	$K\,(m\,s^{-1}) = \left(k_l K_{eq} k_g\right)/\left(K_{eq} k_g + k_l\right)$ Where: $K_{eq} = H/(RT)$
11	$N\,(g\,s^{-1}) = (1 - C_t/C_o)\,V\,C_O/t$ Where: $C_t/C_o = exp[-K\,A\,t/V]$

Source: table 4.3-1 in U.S. EPA (1998). Equations were chosen according to the instruction in Figure 4.3.4 in U.S. EPA (1998). Definitions of parameters are shown in Table A-25.

Table A-25. Definitions of parameters listed in Table A-24.

Parameters	Definition	Units
A	Wastewater surface area	m^2
C_o	Initial concentration of constituent in the liquid phase	$g\ m^{-3}$
C_t	Concentration of constituent in the liquid phase at time = t	$g\ m^{-3}$
D_a	Diffusivity of constituent in air	$cm^2\ s^{-1}$
d_e	Effective diameter	m
D	Wastewater depth	m
D_{ether}	Diffusivity of ether in water	$cm^2\ s^{-1}$
D_w	Diffusivity of constituent in water	$cm^2\ s^{-1}$
F/D	Fetch to depth ratio, d_e/D	dimensionless
H	Henry's law constant of constituent	$atm\text{-}m^3\ gmol^{-1}$
K	Overall mass transfer coefficient for transfer of constituent from liquid phase to gas phase	$m\ s^{-1}$
K_{eq}	Equilibrium constant or partition coefficient	dimensionless
k_g	gas phase mass transfer coefficient	$m\ s^{-1}$
k_l	liquid phase mass transfer coefficient	$m\ s^{-1}$
N	Emissions	$g\ s^{-1}$
R	Universal gas constant	$atm\text{-}m^3\ (gmol\text{-}k)^{-1}$
Sc_G	Schmidt number on gas side	dimensionless
Sc_L	Schmidt number on liquid side	dimensionless
T	Temperature of water	Kelvin(K)
t	Residence time of disposal	s
U^*	Friction velocity	$m\ s^{-1}$
U_{10}	Wind speed at 10 m above the liquid surface	$m\ s^{-1}$
V	Wastewater volume	m^3
ρ_a	Density of air	$g\ cm^{-3}$
ρ_L	Density of water	$g\ m^{-3}$
μ_a	Viscosity of air	$g\ (cm\ s)^{-1}$
μ_L	Viscosity of water	$g\ (cm\ s)^{-1}$

Sources: table 4.3-2 in U.S. EPA (1998).

Table A-26. Percentiles (25th, 50th, and 75th) of the 9 input parameters.

Percentiles	I ($W\ (m^2\ day)^{-1}$)	T_{AX} (°C)	T_{AN} (°C)	t_{fd} [a]	V_{ca} (gal)	a [b]	L (m) [b]	W (m) [b]	H_S (m) [b]	H_L/H_S [b]
25	6,340	16.1	0.6	1	3,693	0.153	1.098	0.918	1.215	0.675
50	8,945	25.0	9.4	3	11,919	0.170	1.220	1.020	1.350	0.750
75	10,885	32.2	17.8	6	32,832	0.187	1.342	1.122	1.485	0.825

[a] the percentiles were obtained from 40,937 wells which reported both of fracturing starting and ending dates.
[b] assuming 25th percentile = 50th percentile × 0.9, 75th percentile = 50th percentile × 1.1.

Table A-27. Frequency of t_{fd} used for Monte Carlo Simulations.

Fracturing Days	Wells [a]		Frequency [b]
	Frequency	percentages	
1	12,631	30.85	3085
2	7,151	17.47	1747
3	4,411	10.78	1078
4	3,335	8.15	815
5	2,833	6.92	692
6	2,331	5.69	569
7	1,903	4.65	465
8	1,546	3.78	378
9	1,246	3.04	304
10	960	2.35	235
11	836	2.04	204
12	665	1.62	162
13	642	1.57	157
14	447	1.09	109
Total	40,937	100.00	10,000

[a] 40,937 wells which reported both of fracturing starting and ending dates, and were fractured within 14 days. [b] frequency in 10,000 simulation of Monte Carlo Analysis.

Table A-28. Organics added into hydraulic fracturing fluids and also belong to the group of UVCB in TSCA.

CASNR	Substance Names	Boiling Points [a]	Henry's law constants [b]
119345-03-8	Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated	787.59	1.59E-14
119345-04-9	Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated, sodium salt	935.43	1.61E-14
127087-87-0	Poly(oxy-1,2-ethanediyl), à-(4-nonylphenyl)- -hydroxy-, branched	496.70	9.61E-15
147732-60-3	Benzene, 1,1'-oxybis-, sec-hexyl derivs., sulfonated, sodium salts	673.21	2.52E-10
61788-46-3	Amines, coco alkyl	254.63	1.71E-04
61788-62-3	Amines, dicoco alkylmethyl	403.71	1.86E-02
61788-90-7	Amines, coco alkyldimethyl, N-oxides	426.62	6.61E-11
61788-93-0	Amines, coco alkyldimethyl	260.12	8.25E-04
61789-18-2	Quaternary ammonium compounds, coco alkyltrimethyl, chlorides	453.47	9.42E-11
61789-40-0	1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl	650.63	6.19E-21
61789-68-2	Quaternary ammonium compounds, benzylcoco alkylbis(hydroxyethyl), chl	647.74	1.79E-17
61789-71-7	Quaternary ammonium compounds, benzylcoco alkyldimethyl, chlorides	537.63	7.61E-12
61789-76-2	Amines, dicoco alkyl	402.53	8.48E-03
61789-77-3	Quaternary ammonium compounds, dicoco alkyldimethyl, chlorides	581.12	2.13E-09
61790-12-3	Fatty acids, tall-oil	385.62	4.48E-05
61790-33-8	Amines, tallow alkyl	345.55	8.24E-04
61790-57-6	Amines, coco alkyl, acetates	453.86	1.08E-13
61790-60-1	Amines, tallow alkyl, acetates	527.06	5.18E-13
61790-85-0	Amines, N-tallow alkyltrimethylenedi-, ethoxylated	802.72	4.86E-16
61791-00-2	Fatty acids, tall-oil, ethoxylated	548.67	4.06E-14
61791-08-0	Fatty acids, coco, reaction products with ethanolamine, ethoxylated	804.80	2.76E-29
61791-10-4	Quaternary ammonium compounds, coco alkylbis(hydroxyethyl)methyl, eth	739.90	2.01E-25
61791-14-8	Amines, coco alkyl, ethoxylated	470.99	1.06E-15
61791-26-2	Amines, tallow alkyl, ethoxylated	544.19	5.11E-15
61791-29-5	Fatty acids, coco, ethoxylated	475.47	8.44E-15
61791-44-4	Ethanol, 2,2'-iminobis-, N-tallow alkyl derivs.	459.39	9.35E-09
61791-63-7	Amines, N-coco alkyltrimethylenedi-	459.03	3.37E-06
63148-52-7	Siloxanes and Silicones, di-Me, Me Ph	374.57	2.18E-03
63148-62-9	Siloxanes and Silicones, di-Me	184.70	1.70E+01
64741-44-2	Distillates (petroleum), straight-run middle	185.61	1.93E+00
64741-67-9	Residues (petroleum), catalytic reformer fractionator	327.31	4.24E-05
64741-68-0	Naphtha (petroleum), heavy catalytic reformed	231.64	4.23E-04
64741-85-1	Raffinates (petroleum), sorption process	279.56	4.34E+00
64741-86-2	Distillates (petroleum), sweetened middle	205.71	8.18E+00
64741-88-4	Distillates (petroleum), solvent-refined heavy paraffinic	436.47	1.53E+03
64741-92-0	Naphtha (petroleum), solvent-refined heavy	142.69	3.40E+00
64742-46-7	Distillates (petroleum), hydrotreated middle	260.59	1.26E+01
64742-47-8	Distillates (petroleum), hydrotreated light	205.71	8.18E+00
64742-48-9	Naphtha (petroleum), hydrotreated heavy	142.69	3.40E+00
64742-52-5	Distillates (petroleum), hydrotreated heavy naphthenic	340.71	1.79E+01
64742-60-5	Hydrocarbon waxes (petroleum), hydrotreated microcryst.	378.45	3.72E+02
64742-65-0	Distillates (petroleum), solvent-dewaxed heavy paraffinic	442.75	4.57E-07
64742-81-0	Kerosine (petroleum), hydrodesulfurized	205.71	8.18E+00

Table A-28. Organics added into hydraulic fracturing fluids and also belong to the group of UVCB in TSCA. (Continued)

CASNR	Substance Names	Boiling Points [a]	Henry's law constants [b]
64742-88-7	Solvent naphtha (petroleum), medium aliph.	164.60	5.15E+00
64742-89-8	Solvent naphtha (petroleum), light aliph.	96.16	2.00E+00
64742-94-5	Solvent naphtha (petroleum), heavy arom.	231.64	4.23E-04
64742-95-6	Solvent naphtha (petroleum), light arom.	231.64	4.23E-04
64742-96-7	Solvent naphtha (petroleum), heavy aliph.	224.91	2.88E+00
64743-01-7	Petrolatum (petroleum), oxidized	481.63	1.01E-10
64743-02-8	Alkenes, C>10 .alpha.-	162.99	5.41E-01
64771-72-8	Paraffins (petroleum), normal C5-20	164.60	5.15E+00
65071-95-6	Tall oil, ethoxylated	548.67	4.06E-14
66455-14-9	Alcohols, C12-13, ethoxylated	261.25	2.58E-02
66455-15-0	Alcohols, C10-14, ethoxylated	225.63	1.47E-02
67762-38-3	Fatty acids, C16-18 and C18-unsatd., Me esters	352.56	1.44E-02
67762-90-7	Siloxanes and Silicones, di-Me, reaction products with silica	644.90	3.50E-33
67784-80-9	Soybean oil, Me ester	356.14	1.26E-02
68002-97-1	Alcohols, C10-16, ethoxylated	402.88	2.01E-12
68037-13-8	1-Propene, 2-methyl-, trimer, sulfurized	386.98	6.18E-01
68037-59-2	Siloxanes and Silicones, di-Me, Me hydrogen	220.81	3.02E-01
68081-81-2	Benzenesulfonic acid, mono-C10-16-alkyl derivs., sodium salts	660.62	6.29E-08
68081-98-1	Sulfuric acid, mono-C14-18-alkyl esters, sodium salts	649.06	8.77E-08
68131-39-5	Alcohols, C12-15, ethoxylated	461.35	5.51E-14
68131-40-8	Alcohols, C11-15-secondary, ethoxylated	442.75	4.15E-14
68131-73-7	Amines, polyethylenepoly-	366.69	8.36E-24
68140-01-2	Amides, coco, N-[3-(dimethylamino)propyl]	407.12	3.65E-10
68155-06-6	Amides, C12-18, N,N-bis(hydroxyethyl)	419.03	1.63E-12
68155-09-9	Amides, coco, N-[3-(dimethylamino)propyl], N-oxides	608.58	3.81E-20
68155-20-4	Amides, tall-oil fatty, N,N-bis(hydroxyethyl)	503.83	1.04E-11
68155-39-5	Amines, C14-18 and C16-18-unsatd. alkyl, ethoxylated	357.61	7.25E-06
68187-17-7	Sulfuric acid, mono-C6-10-alkyl esters, ammonium salts	465.45	2.84E-16
68188-40-9	Fatty acids, tall-oil, reaction products with acetophenone,formaldehy	713.25	1.57E-16
68213-23-0	Alcohols, C12-18, ethoxylated	484.56	9.71E-14
68308-35-0	Shellac, ammonium salt	587.01	6.80E-21
68308-89-4	Fatty acids, C18-unsatd., dimers, ethoxylated propoxylated	982.18	4.07E-23
68334-30-5	Fuels, diesel	243.20	9.20E+00
68391-01-5	Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl,chlorides	560.84	1.34E-11
68391-11-7	Pyridine, alkyl derivs.	179.83	1.14E-05
68410-62-8	Naphthenic acids, ethoxylated	446.02	3.08E-14
68424-85-1	Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl,chlorides	560.84	1.34E-11
68439-45-2	Alcohols, C6-12, ethoxylated	414.94	1.77E-14
68439-46-3	Alcohols, C9-11, ethoxylated	438.14	3.13E-14
68439-50-9	Alcohols, C12-14, ethoxylated	261.25	2.58E-02
68439-51-0	Alcohols, C12-14, ethoxylated propoxylated	261.25	2.58E-02
68439-57-6	Sulfonic acids, C14-16-alkane hydroxy and C14-16-alkene, sodium salts	611.28	6.68E-07
68439-70-3	Amines, C12-16-alkyldimethyl	292.24	1.45E-03
68439-72-5	Amines, C8-18 and C18-unsatd. alkyl, ethoxylated	600.43	5.45E-16
68440-27-7	Fatty acids, tall-oil, sulfurized	759.14	1.19E-09
68526-83-0	Alcohols, C7-9-iso-, C8-rich	188.52	9.21E-05
68526-85-2	Alcohols, C9-11-iso-, C10-rich	269.99	9.51E-07

Table A-28. Organics added into hydraulic fracturing fluids and also belong to the group of UVCB in TSCA. (Continued)

CASNR	Substance Names	Boiling Points [a]	Henry's law constants [b]
68526-86-3	Alcohols, C11-14-iso-, C13-rich	279.35	1.28E-04
68551-12-2	Alcohols, C12-16, ethoxylated	261.25	2.58E-02
68551-19-9	Alkanes, C12-14-iso-	213.44	1.24E+01
68551-20-2	Alkanes, C13-16-iso-	171.52	3.46E+00
68584-22-5	Benzenesulfonic acid, C10-16-alkyl derivs.	436.72	3.56E-08
68584-25-8	Benzenesulfonic acid, C10-16-alkyl derivs., compds. with triethanolam	564.60	1.77E-14
68603-42-9	Amides, coco, N,N-bis(hydroxyethyl)	430.64	2.16E-12
68604-75-1	Fatty acids, coco, reaction products with diethylenetriamineand soya	1005.42	3.51E-30
68607-19-2	Pyridine, alkyl derivs., hydrochlorides	229.36	1.26E-11
68607-28-3	Quaternary ammonium compounds, (oxydi-2,1-ethanediyl)bis[coco alkyldi	839.87	2.49E-15
68647-72-3	Terpenes and Terpenoids, sweet orange-oil	167.66	3.19E-02
68648-87-3	Benzene, C10-16-alkyl derivs.	324.45	1.34E-01
68649-37-6	Phosphonic acid, [iminobis(methylene)]bis-, N-coco alkyl derivs., amm	480.00	1.81E-36
68649-44-5	Ethanol, 2-amino-, reaction products with ammonia, by-products from,	367.04	7.99E-19
68909-18-2	Pyridinium, 1-(phenylmethyl)-, Et Me derivs., chlorides	338.87	1.96E-11
68909-77-3	Ethanol, 2,2'-oxybis-, reaction products with ammonia, morpholine der	354.99	2.47E-18
68937-55-3	Siloxanes and Silicones, di-Me, 3-hydroxypropyl Me, ethoxylated propo	458.67	4.30E-14
68937-66-6	Alcohols, C6-12, ethoxylated propoxylated	397.19	1.77E-14
68951-67-7	Alcohols, C14-15, ethoxylated	293.25	4.55E-02
68956-79-6	Quaternary ammonium compounds, C12-18-alkyl[(ethylphenyl)methyl]dimet	553.84	1.34E-11
69011-36-5	Poly(oxy-1,2-ethanediyl), à-tridecyl- -hydroxy-, branched	444.97	7.32E-14
69227-22-1	Alcohols, C10-16, ethoxylated propoxylated	225.63	1.47E-02
70592-80-2	Amines, C10-16-alkyldimethyl, N-oxides	403.41	3.75E-11
70851-07-9	Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with c	656.61	1.19E-13
70851-08-0	Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with s	769.01	8.86E-21
71011-03-5	Amines, ditallow alkyl, acetates	738.43	1.02E-10
71060-57-6	Alcohols, C8-10, ethoxylated	186.40	8.32E-03
73138-29-1	Alkanes, C10-18	164.60	5.15E+00
73296-89-6	Sulfuric acid, mono-C12-16-alkyl esters, sodium salts	588.52	1.84E-07
78330-19-5	Alcohols, C7-9-iso-, C8-rich, ethoxylated	400.95	1.77E-14
78330-20-8	Alcohols, C9-11-iso-, C10-rich, ethoxylated	202.42	1.47E-02
78330-21-9	Alcohols, C11-14-iso-, C13-rich, ethoxylated	257.75	3.43E-02
78330-23-1	Alcohols, C11-14-iso-, C13-rich, ethoxylated propoxylated	257.75	3.43E-02
8001-26-1	Linseed oil	847.11	5.05E-04
8001-31-8	Coconut oil	632.85	1.52E-05
8001-79-4	Castor oil	904.15	1.89E-10
8002-05-9	Petroleum	357.63	1.59E+02
8002-09-3	Oils, pine	209.98	1.38E-05
8002-26-4	Tall oil	429.71	2.69E-07
8002-43-5	Lecithins	480.00	2.54E-22
8002-74-2	Paraffin waxes and Hydrocarbon waxes	333.99	9.02E+01
8008-20-6	Kerosine (petroleum)	205.71	8.18E+00
8012-95-1	Paraffin oils	205.71	8.18E+00
8017-16-1	Polyphosphoric acids	480.00	6.20E-27
8032-32-4	Ligroine	119.87	3.21E+00
8042-47-5	White mineral oil (petroleum)	119.87	3.21E+00
8050-09-7	Rosin	394.94	6.76E-06

Table A-28. Organics added into hydraulic fracturing fluids and also belong to the group of UVCB in TSCA. (Continued)

CASNR	Substance Names	Boiling Points [a]	Henry's law constants [b]
8052-41-3	Stoddard solvent	164.60	5.15E+00
84133-50-6	Alcohols, C12-14-secondary, ethoxylated	454.36	5.51E-14
84852-15-3	Phenol, 4-nonyl-, branched	299.32	4.30E-06
90218-35-2	Benzenesulfonic acid, dodecyl-, branched, compd. with 2-propanamine	431.95	6.27E-08

[a] unit: °C; [b] unit: atm-m^3 mol^{-1} at 25 °C. Data source of boiling points and henry's law constants: Estimation programs interface (EPI Suite™) by U.S. EPA (2015).

Table A-29. Organics added into hydraulic fracturing fluids considered as candidate substances for the Priority List of Hazardous Substances (ATSDR, 2013).

CASRN	Substance Names	Num. of Wells [a]	Median emissions (kg well^{-1} day^{-1})	Total emissions (kg)	Ranks [b]	Toxicity Points [c]
NMVOCs						
100-52-7	Benzaldehyde	1	4.06E-05	2.84E-04	545	53
107-13-1	2-Propenenitrile	5	3.56E-02	8.61E-01	264	178
107-41-5	2,4-Pentanediol, 2-methyl-	3	6.01E-05	1.02E-03	699	0
111-27-3	1-Hexanol	2	7.37E-05	5.90E-04	667	10
111-44-4	Ethane, 1,1'-oxybis 2-chloro-	7	1.81E-03	1.78E-01	84	400
141-78-6	Acetic acid ethyl ester	87	6.76E-03	9.55E-01	411	10
542-75-6	1-Propene, 1,3-dichloro-	6	3.84E-05	8.66E-04	446	178
62-53-3	Benzenamine	25	1.86E-04	3.35E-01	413	10
62-56-6	Thiourea	57	8.89E-07	7.04E-02	365	400
68334-30-5	Fuels, diesel	2	4.53E-05	3.63E-04	783	0
71-43-2	Benzene	10	8.71E-02	2.55E+00	6	400
75-09-2	Methane, dichloro-	6	1.17E-03	2.93E-02	86	53
75-52-5	Methane, nitro-	25	5.25E-03	3.08E+01	615	53
8012-95-1	Paraffin oils	17	2.19E-03	1.74E-01	783	0
8032-32-4	Ligroine	95	8.11E-03	3.75E+00	783	0
91-22-5	Quinoline	33	6.72E-07	1.00E-03	645	10
98-01-1	2-Furancarboxaldehyde	1	8.32E-04	3.33E-03	673	10
NVOCs						
117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	15	4.48E-10	5.33E-08	76	178
126-73-8	Phosphoric acid tributyl ester	1	2.99E-05	8.97E-05	522	178
60-00-4	Glycine, N,N -1,2-ethanediylbis[N-(carboxymethyl)-	1	7.51E-15	6.76E-14	680	10
80-05-7	Phenol, 4,4 -(1-methylethylidene)bis-	24	2.58E-08	1.61E-06	615	53
8002-05-9	Petroleum	60	1.11E-05	1.45E-03	783	0
85-44-9	1,3-Isobenzofurandione	15	1.77E-09	1.06E-05	673	10
88-99-3	1,2-Benzenedicarboxylic acid	5	8.27E-08	1.21E-06	699	0
9002-88-4	Ethene, homopolymer	1	1.31E-13	1.31E-13	699	0
9002-93-1	Octoxynol	6	8.27E-03	2.34E-01	680	10

[a] number of wells reported the organic in hydraulic fracturing fluids with concentration > 0; [b] the top 275 ranked chemicals were considered as the Priority List of Hazardous Substances; [c] the maximum point in toxicity was 600.

Table A-30. Vapor pressures and Henry's Law Constants of xylenes (total), toluene, benzene, and ethylbenzene at 25 degree C obtained from EPI Suite™ (U.S. EPA, 2015).

Chemicals	CASRN	Vapor Pressure (mm Hg)	Henry's Law Constants (atm-m^3 mole^{-1})
Xylenes(total)	1330-20-7	6.81	5.08E-03
Toluene	108-88-3	23.7	6.44E-03
Benzene	71-43-2	87.2	5.51E-03
Ethylbenzene	100-41-4	7.59	7.82E-03

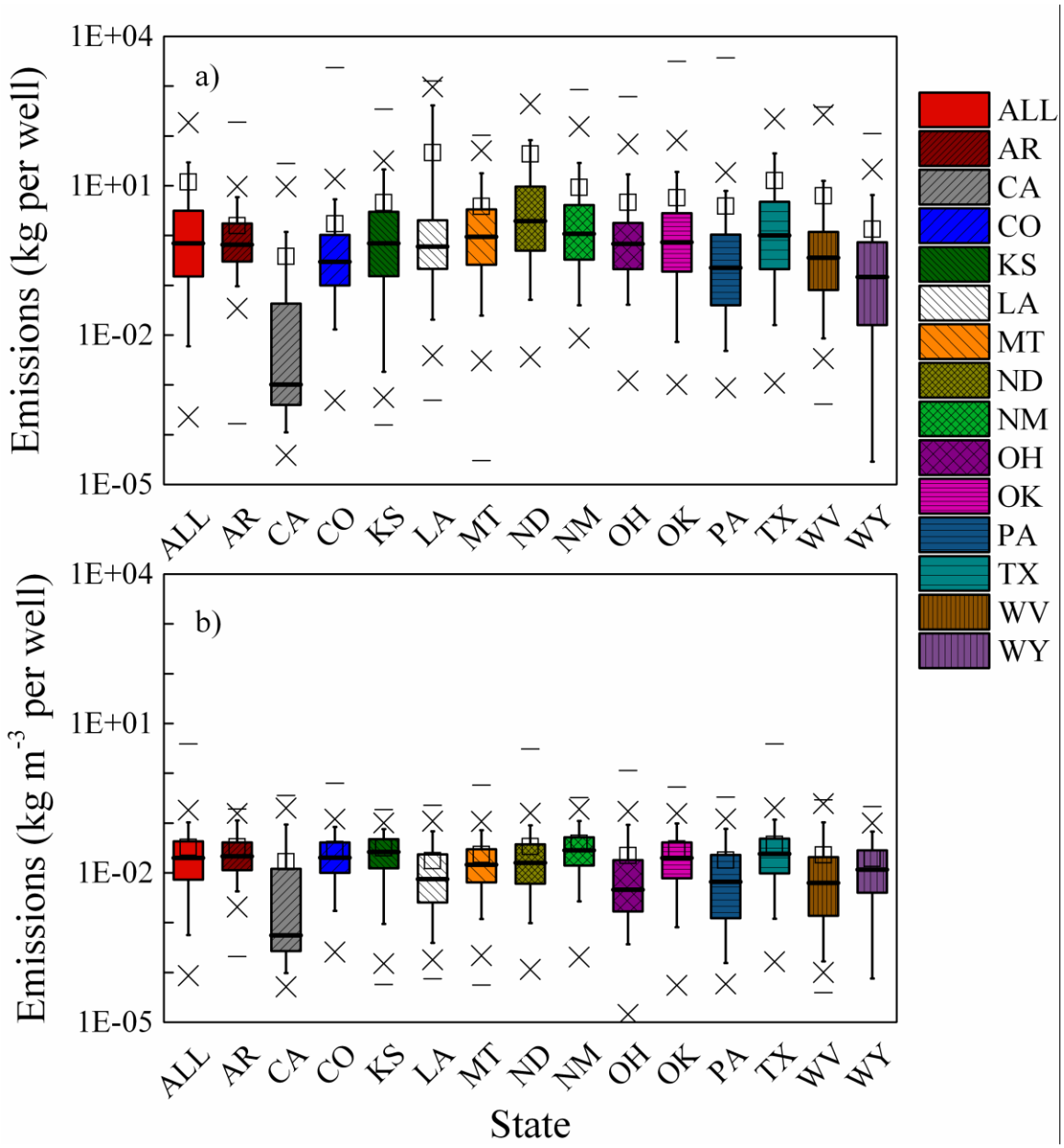

Figure A-12. Emissions of well in the 14 states that were used for this study: a) emission in each well (kg per well) b) emission normalized by the volume of the chemical additives in each well (kg m^{-3} per well). Each data sample represents the corresponding value of a well. The emissions in all the 14 states with a median value of 0.700 kg per well and 0.020 kg m^{-3} per well after being normalized by the volume of chemical additives.

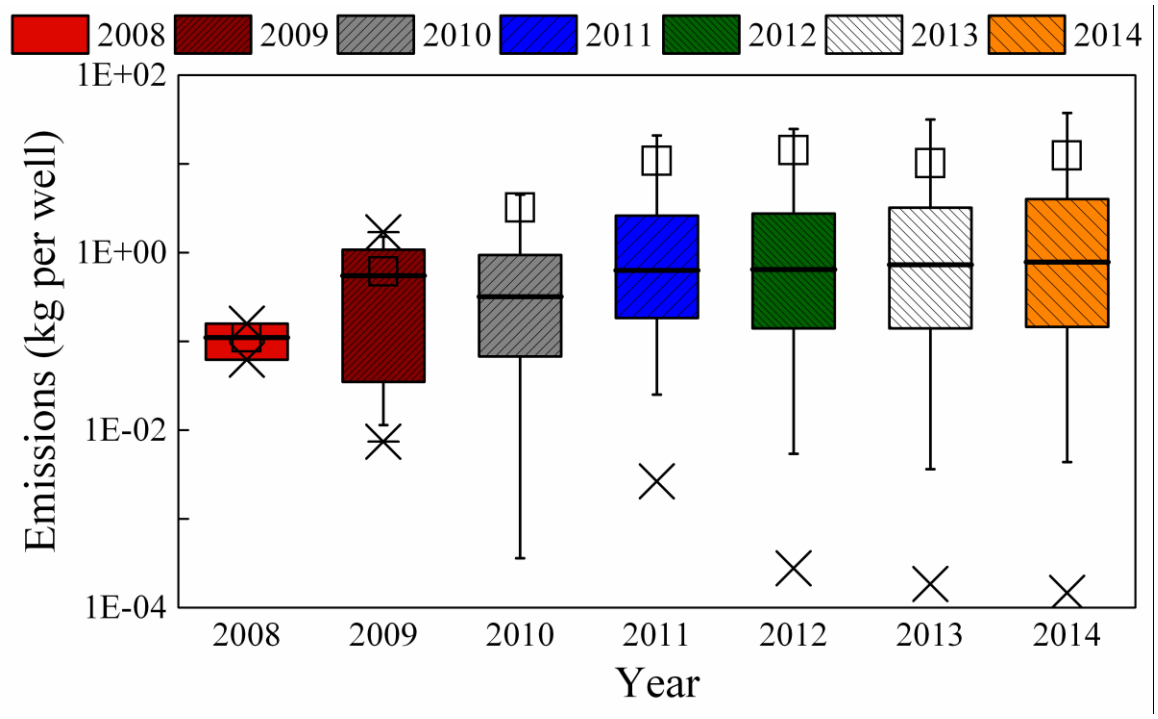

Figure A-13. Time series analysis for the emissions at each well (kg per well).

In Figure A-14.a, the 50th percentile in median organic emissions was 9.22×10^{-9} kg per well. The smallest and largest values in the 50th percentiles were 1.28×10^{-8} kg per well in Colorado and 4.16×10^{-6} kg per well in Ohio. In Fig. S4b, the 50th percentile in median organic emissions was 2.39×10^{-10} kg m^{-3} per well, with the smallest value of 1.55×10^{-10} kg m^{-3} per well in North Dakota and the largest value of 2.74×10^{-8} kg m^{-3} per well in Arkansas. Jeon et al. (2009) reported the emissions of methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and trimethylamine from a WWTP were 1.2×10^{-8}, 3.4×10^{-8}, 2.7×10^{-7}, and 6.0×10^{-9} kg m^{-3}.

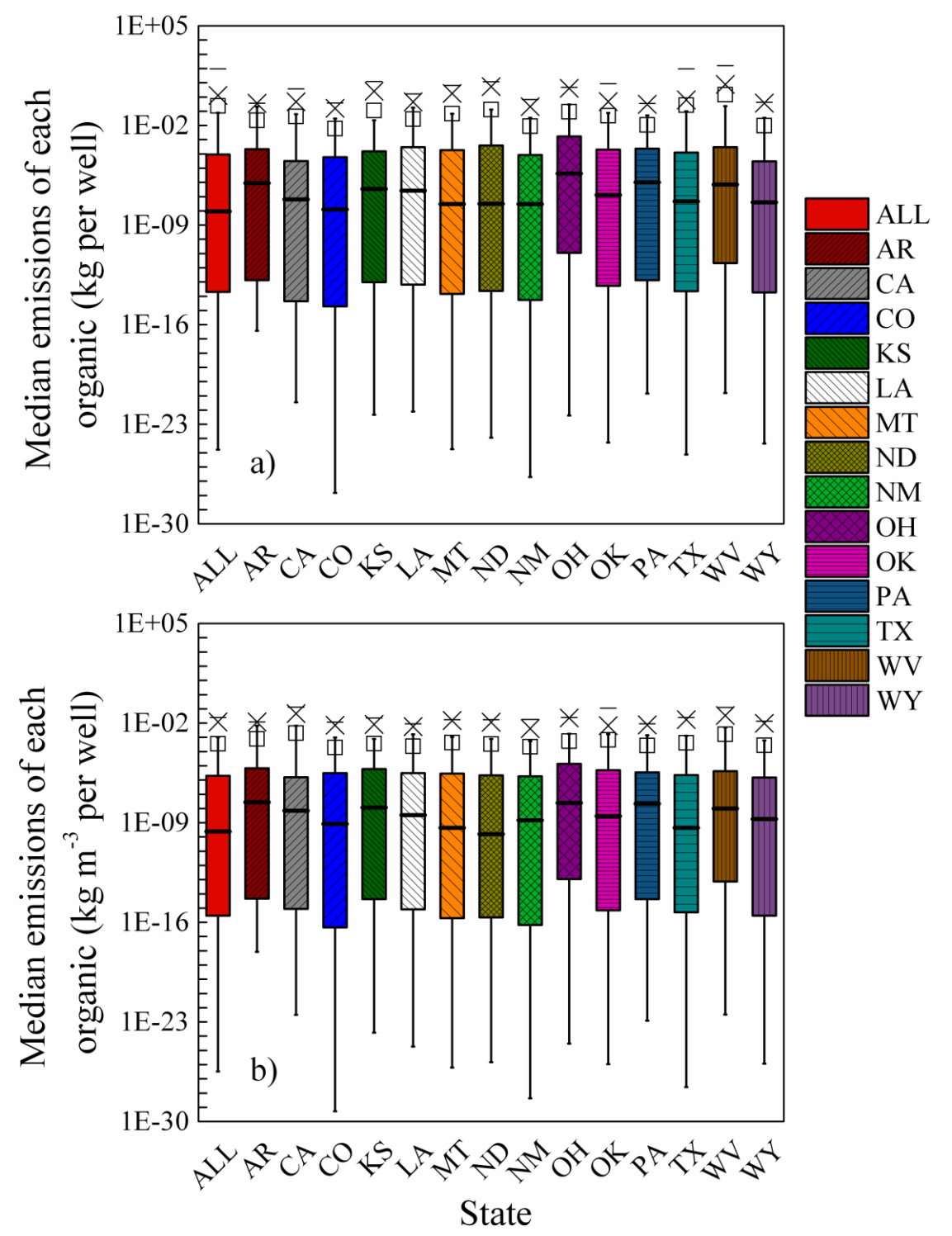

Figure A-14. Median emissions for the organic compounds used in hydraulic fracturing fluids: a) Emission of the organics in each well (kg per well) and b) median emissions of the organics normalized by the volume of chemical additives in each well (kg m^{-3} per well).

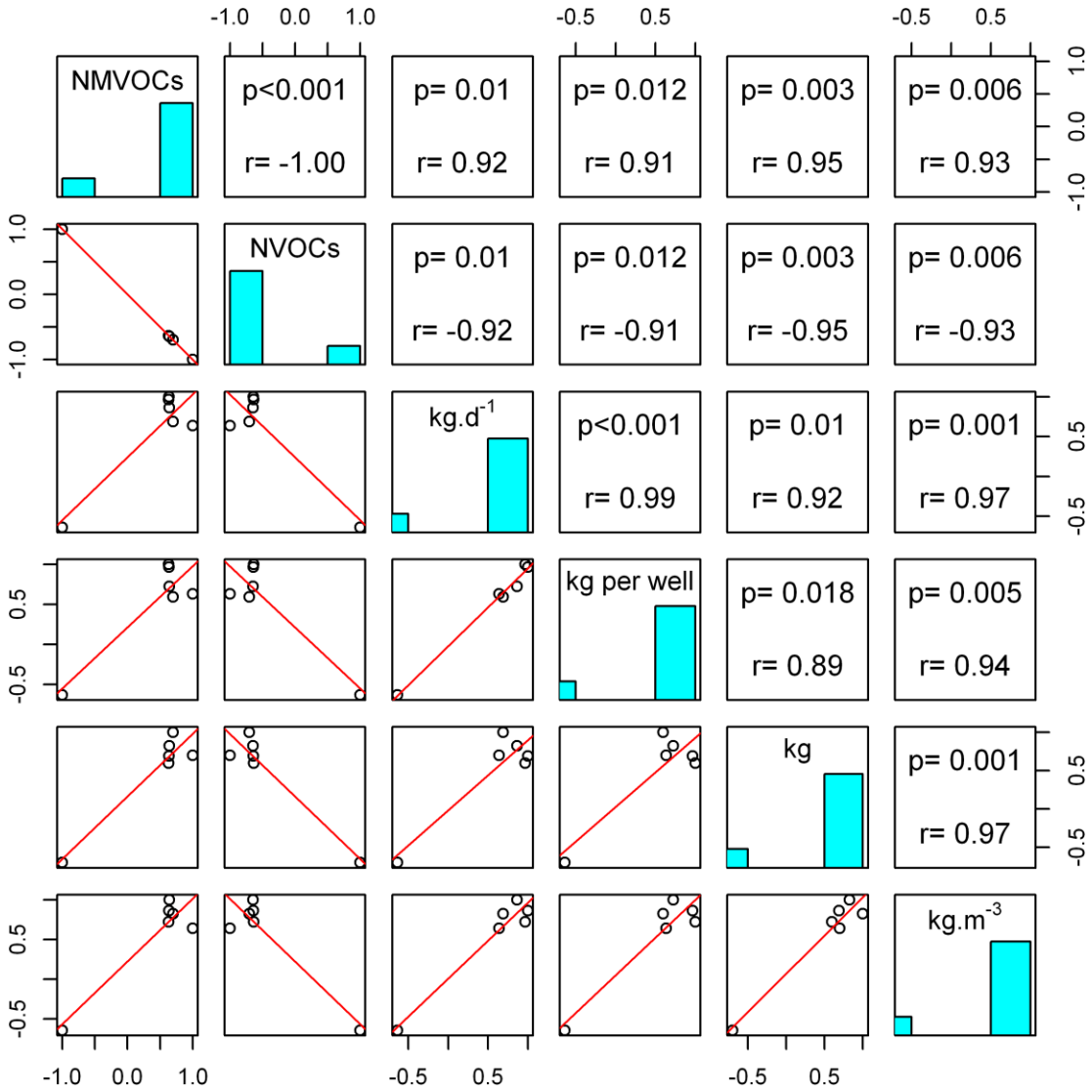

Figure A-15. The relationship between the percentages of NMVOCs and NVOCs, the 50th percentiles of the median emissions (kg d^{-1} per well, kg per well, and kg m^{-3} per well) and the total emissions (kg) from the wells in this study related to the different parameters. The correlation analysis was carried out with the Pearson method and plotted in the R version 3.2.0.

The 50th percentile of median emissions for NMVOCs and NVOCs was 2.64×10^{-4} and 4.22×10^{-13} kg per well (Fig. S6a), and 8.86×10^{-6} and 1.35×10^{-14} kg m^{-3} per well (Figure A-16.b). The 50th percentile of the total emissions for NMVOCs and NVOCs was 0.679 and 6.89×10^{-10} kg (Figure A-16.c).

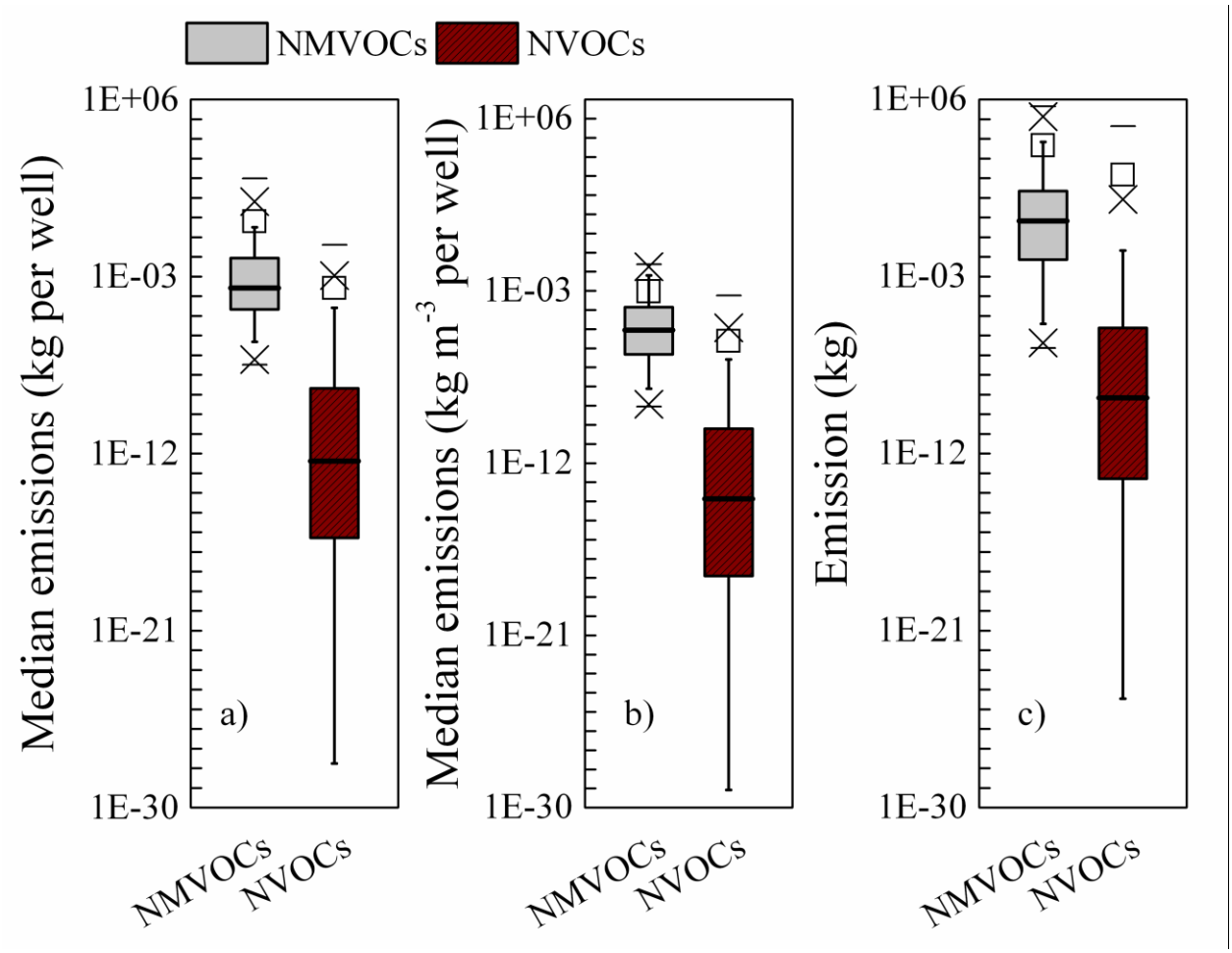

Figure A-16. Emissions from NMVOCs and NVOCs: a) median emissions of each organic from each well (kg per well); b) median emissions of each organic normalized by the volume of the chemical additives from each well (kg m^{-3} per well); and c) emissions of each organic in all the wells used in this study (kg). Each data sample represents the corresponding value of an organic compound.

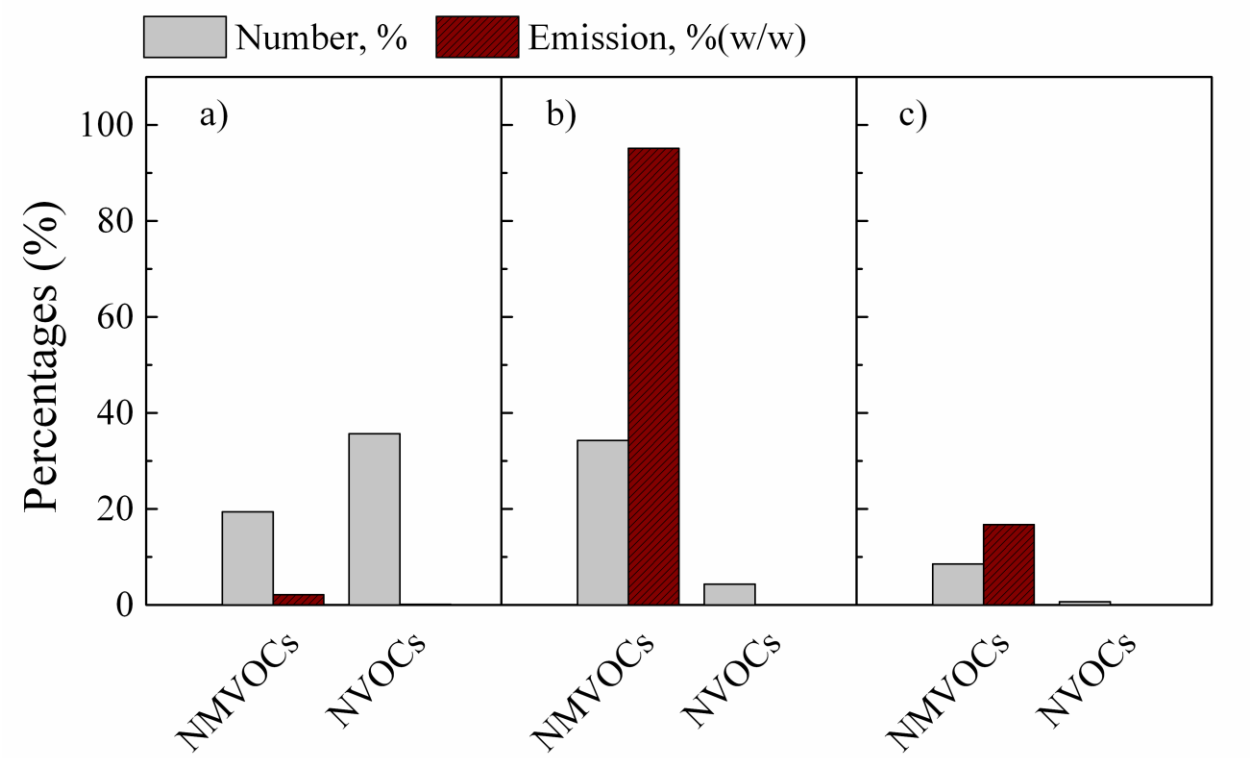

Figure A-17. Percentage of NMVOCs and NVOCs and their emissions: a) unknown or variable composition, complex reaction products and biological materials (UVCB); b) candidate substances for the Priority List of Hazardous Substances from Agency for Toxic Substances & Disease Registry (ATSDR); and c) Carcinogenic substances listed by the National Toxicology Program of the U.S. Department of Health and Human Services (NTP, 2014).

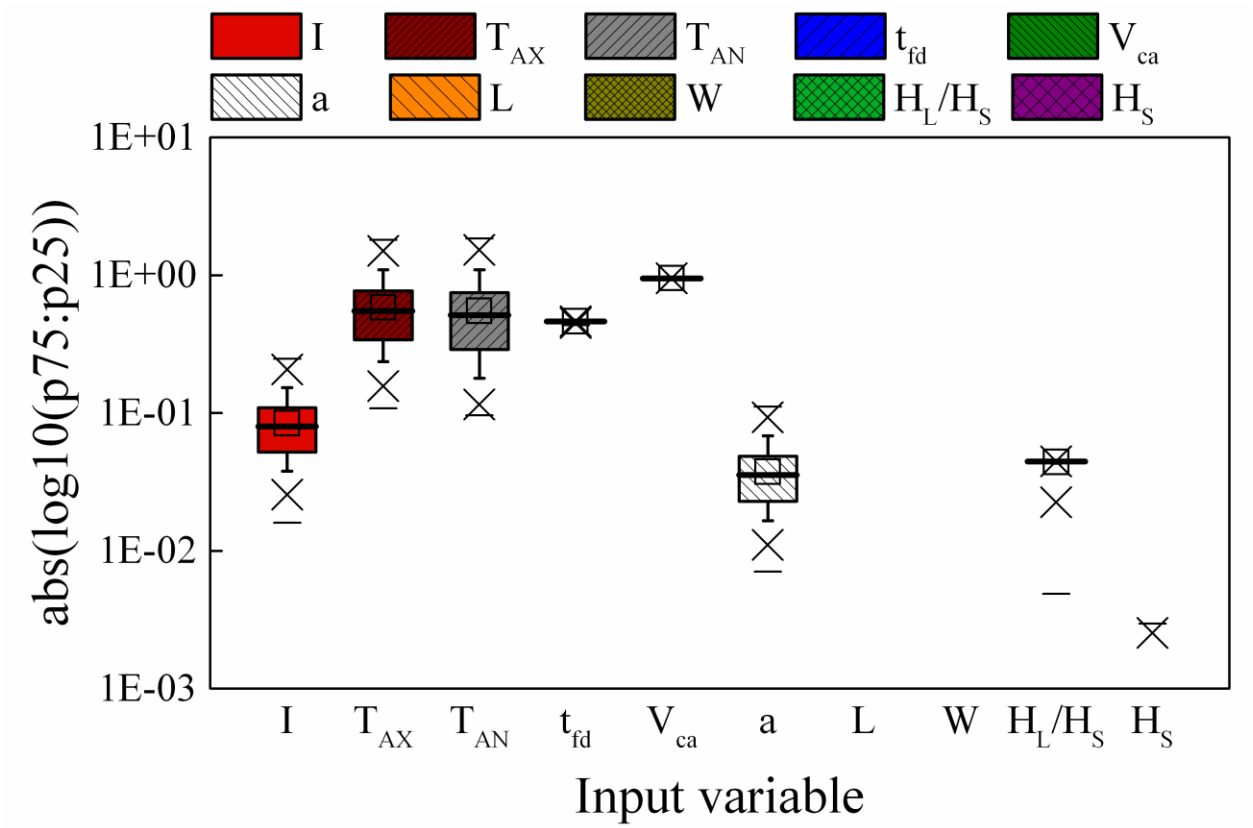

Figure A-18. Sensitivity analysis of the input parameters based on the AP-42 model for each organic compound. Each data sample represents the abs($\log_{10}$(p75:p25)) value for the parameters that affect the model for each organic compound. A higher abs($\log_{10}$(p75:p25)) value indicates more sensitivity of a compound toward a parameter.

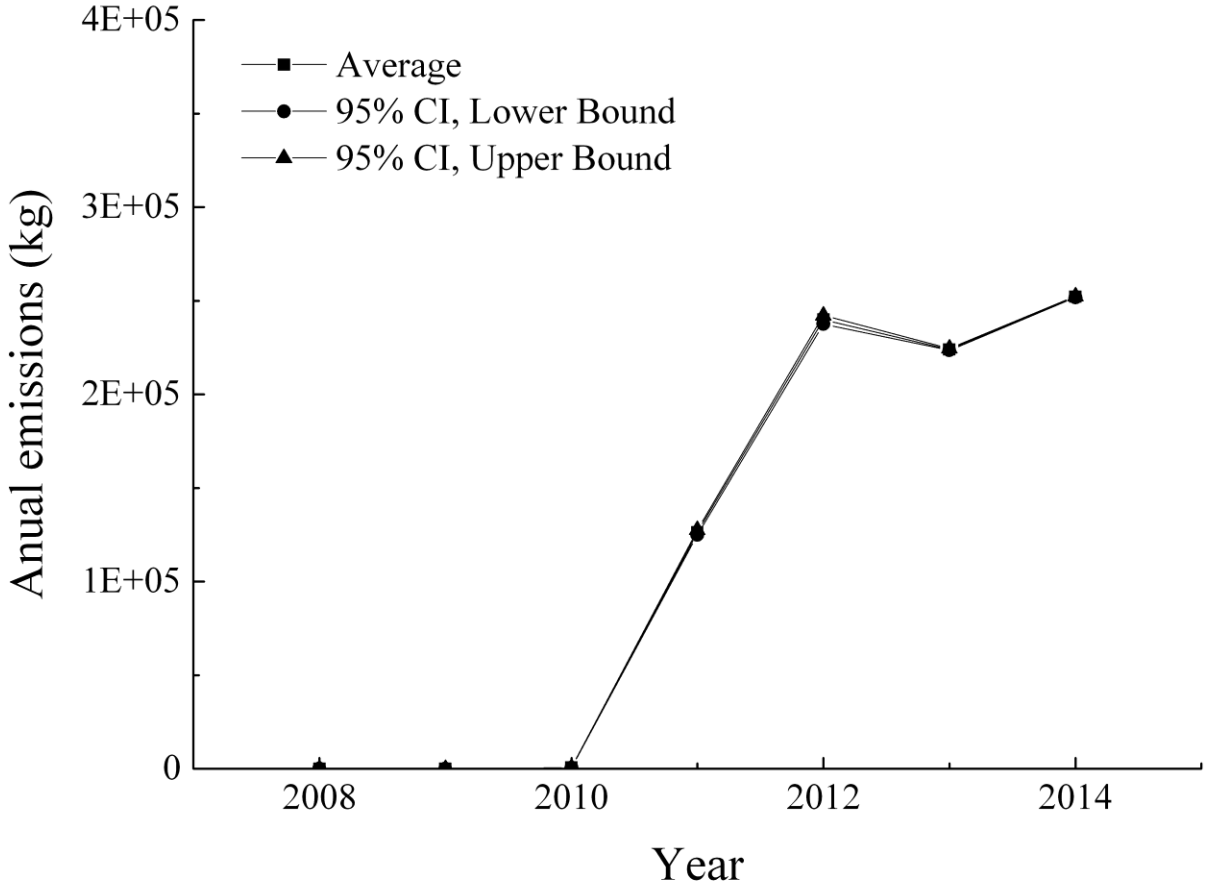

Figure A-19. Monte Carlo simulations for the effect of the uncertainties from H_L/H_S, a, I, T_{AX}, T_{AN}, and t_{fd} on the annual total emissions from 2008 to 2014.

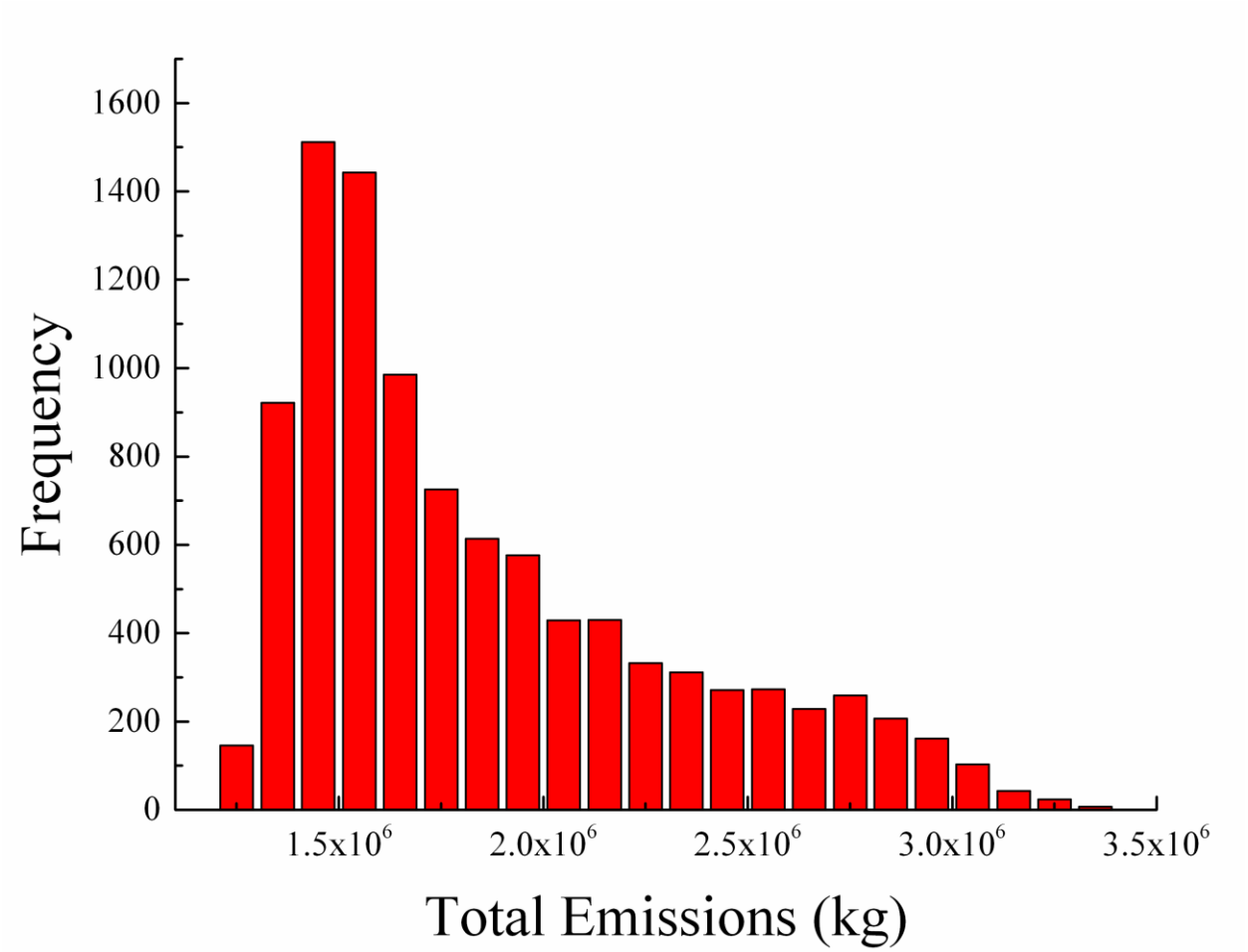

Figure A-20. The distribution of total emissions from the 10,000 runs of Monte Carlo Simulation for uncertainty analysis.

Appendix D

Equation A-36

Non-cancer exposure risks in hydraulic fracturing wells

$$HQ_i = \sum_{j=1}^{n} HQ_j$$

Where: HQ_i, hazard quotient in the i-th well; HQ_j, hazard quotient of the j-th organic; n, the number of organics in chemical additives used in the i-th well.

Equation A-37

Cancer exposure risks in hydraulic fracturing wells

$$Risk_i = \sum_{j=1}^{n} Risk_j$$

Where: $Risk_i$, cancer exposure risk in the i-th well; $Risk_j$, cancer exposure risk of the j-th organic; n, the number of organics in chemical additives used in the i-th well.

Equation A-38

Gaussian dispersion model (De Visscher, 2013)

$$C(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z u} exp\left[\frac{-y^2}{2\sigma_y^2}\right]\left\{exp\left[\frac{-(z-H)^2}{2\sigma_z^2}\right] + exp\left[\frac{-(z+H)^2}{2\sigma_z^2}\right]\right\}$$

Where: x, distance in the downwind, m; y, distance in the crosswind, m; z, distance in the vertical direction, m; H, the effective stack height which is the sum of stack height and plume rise, m; u, the wind speed at the stack height, m s^{-1}; σ_y and σ_z, the standard deviations of the concentration distribution in the crosswind and vertical directions, respectively, m; C (x, y, z), the air concentration at a given position of (x, y, z), g m^{-3}; Q, the source emission rate, g s^{-1}.

Equation A-39

Stagnant two-film model (Bloomdahl et al., 2014)

$$\text{Flux} = \left(\frac{1}{(Z_w/D_w + (Z_a/D_a K'_H))}\right)\left(C_w - \frac{C_a}{K'_H}\right)$$

Where: Z_a, thickness of stagnant layer of air, cm; Z_w, thickness of stagnant layer of water, cm; D_a, diffusivity of substance in air, cm^2 s^{-1}; D_w, diffusivity of substance in water, cm^2 s^{-1}; K_H', Henry's constant, dimensionless; C_a, concentration of substance in air, µg cm^{-3}; C_w, concentration of substance in water, µg cm^{-3}; Flux, µg cm^{-2} s^{-1}.

Equation A-40

Box model (Bloomdahl et al., 2014)

$$C_i = \frac{E_i}{u \times W \times H}$$

Where: C_i, air concentration of chemical i, g m^{-3}; E_i, emission of chemical i, g s^{-1}; u, air velocity, u = 4.47 m s^{-1}; W, the width of open flowback pit, W = 125 ft = 38.1 m; H, the height of worker breathing zone, H = 1.67 m.

Table A-31. Volume source inputs in AERMOD are listed (U.S. EPA, 2004b).

Parameters	Units	Descriptives
Vlemis	g s^{-1}	Volume emission rate
Relhgt	m	Release height (center of volume) above ground
Syinit	m	Initial lateral dimension of the volume
Szinit	m	Initial vertical dimension of the volume

Intermediate bulk containers (IBCs) are commonly used as the chemical storage tanks in hydraulic fracturing (shown in Figure 1-3). The dimensions of IBCs are summarized in Table A-23 and were assumed to be 48 × 40 × 53 inches (Length × Width × Height). The ratio of the maximum liquid height to the tank height was assumed as 0.75. Since the chemicals storage tanks were usually placed on the flatbed trucks (shown in Figure 1-3), the release height above ground is equal to half of the maximum liquid height inside the chemical storage tanks plus the bed height of the flatbed trucks. The standard bed height of a flatbed truck, provided by Auction Transportation Solutions (ATS) (http://www.atsauctionlogistics.com/flatbed-specialized.html, accessed on 2016/5/24) is 58-60 inches, therefore, 60 inches was used in this study. The emissions sources were considered as single volume sources and elevated sources on or adjacent to a building. The initial lateral dimension (Syinit) is equal to the length of side divided by 4.3, and initial vertical dimension of the volume (Szinit) is equal to the building height (the bed height of the flatbed trucks) divided by 2.15 (Table A-31and Table A-32). The length of side is the square root of the liquid surface area, which can be obtained by multiplying the surface area of one tank (tank length × tank width) with the number of tanks.

Table A-32. The suggested procedure for estimating volume source inputs (U.S. EPA, 2004b) for AERMOD are list.

Type of Source	Procedure for Obtaining Initial Dimension
(a) Initial Lateral Dimensions (σ_{yo})	
Single Volume Source	σ_{yo} = length of side divided by 4.3
Line Source Represented by Adjacent Volume	σ_{yo} = length of side divided by 2.15
Line Source Represented by Separated Volume	σ_{yo} = center to center distance divided by 4.3
(b) Initial Vertical Dimensions (σ_{zo})	
Surface-Based Source (he ~ 0)	σ_{zo} = vertical dimension of source divided by 2.15
Elevated Source (he > 0) on or Adjacent to a Building	σ_{zo} = building height divided by 2.15
Elevated Source (he >0) not on or Adjacent to a Building	σ_{zo} = vertical dimension of source divided by 4.3

h_e: effective emission height.

Table A-33. Input parameters related to the exposure periods used in Equation 5-2 are listed.

ET (hr•d^{-1})	EF (d yr^{-1})	ED (yr)	AT (hr)	$\frac{ET \times EF \times ED}{AT}$	Notes	Ref.
8	250	25	683,280 (78 yr)	0.073176	Non-cancer and cancer exposure risks on workers in hydraulic fracturing wells	This study
8	5 [a]	39 [b]	6,552 (39 wk)	0.238095	Non-cancer exposure risks on workers in hydraulic fracturing wells	(Bloomdahl et al., 2014)
8	195	0.75	683,280 (78 yr)	0.001712	Cancer exposure risks on workers in hydraulic fracturing wells	(Bloomdahl et al., 2014)
8	250	30	613,200 (70 yr)	0.097847	Non-cancer exposure risks on pertrol station workers	(Kitwattanavong et al., 2013)
8	250	25	613,200 (70 yr)	0.081539	Cancer exposure risks on vehicle inspection workers	(Li et al., 2013)
6 (swine room) 1 (office space)	330	25	613,200 (70 yr)	0.080724 (swine room) 0.013454 (office space)	Cancer exposure risks on vehicle inspection workers	(Akdeniz et al., 2013)
8 (workers) 24 (residents)	225 (workers) 350 (residents)	25 (workers) 26 (residents)	613,200 (70 yr)	0.073386 (workers) 0.356164 (residents)	Cancer exposure risks on workers and residents caused by hydraulic fracturing wells	(Paulik et al., 2015)

[a] unit: d wk^{-1}; [b] unit: wk; ET: Exposure Time; EF: Exposure Frequency; ED: Exposure Duration; AT: Average Time.

Table A-34. Inhalation Reference Concentration (RfC) and Inhalation Unit Risk (IUR) from U.S. EPA's Integrated Risk Information System (IRIS) are listed for 23 organic compounds found in hydraulic fracturing fluids.

Substance Name	CASRN	RfC ($mg\ m^{-3}$)	Inhalation Unit Risk (per $\mu g\ m^{-3}$)
Acetaldehyde	75-07-0	0.009	N/A
Acrylamide	79-06-1	6.00E-03	1.00E-04
Acrylic acid	79-10-7	0.001	N/A
Acrylonitrile	107-13-1	2.00E-03	6.80E-05
Aniline	62-53-3	0.001	N/A
Benzene	71-43-2	3.00E-02	7.80E-06
Bis(chloroethyl)ether	111-44-4	N/A	3.30E-04
Cumene	98-82-8	0.4	N/A
Dichloromethane	75-09-2	0.6	1.00E-08
1,3-Dichloropropene	542-75-6	0.02	4.00E-06
N,N-Dimethylformamide	68-12-2	0.03	N/A
1,4-Dioxane	123-91-1	0.03	5.00E-06
Epichlorohydrin	106-89-8	1.00E-03	1.20E-06
Ethylbenzene	100-41-4	1	N/A
2-Butoxyethanol	111-76-2	1.6	N/A
Formaldehyde	50-00-0	N/A	1.30E-05
Methanol	67-56-1	0.2	N/A
Methyl isobutyl ketone	108-10-1	3	N/A
Naphthalene	91-20-3	0.003	N/A
Propylene glycol monomethyl ether	107-98-2	2	N/A
Propylene oxide	75-56-9	0.03	3.70E-06
Toluene	108-88-3	5	N/A
Xylenes	1330-20-7	0.1	N/A

N/A: not available.

Table A-35. The numbers of wells with minimum, mean and maximum concentrations located in the radial distance are listed.

Radius (m)	Number of Wells		
	Minimum air concentrations [a]	Mean air concentrations [b]	Maximum air concentrations [c]
5	43,396 (60.25 %)	43,396 (60.25 %)	43,396 (60.25 %)
10	20,678 (28.71 %)	20,678 (28.71 %)	20,678 (28.71 %)
20	5,258 (7.30 %)	5,258 (7.30 %)	5,258 (7.30 %)
50	2,376 (3.30 %)	2,376 (3.30 %)	2,376 (3.30 %)
80	242 (0.34 %)	242 (0.34 %)	242 (0.34 %)
120	63 (0.09 %)	63 (0.09 %)	63 (0.09 %)
150	8 (0.01 %)	8 (0.01 %)	8 (0.01 %)
180	1 (0.00 %)	1 (0.00 %)	1 (0.00 %)
1,600 [d]	1 (0.00 %)	1 (0.00 %)	1 (0.00 %)
Total	72,023 (100.00 %)	72,023 (100.00 %)	72,023 (100.00 %)

[a] using the minimum air concentrations at each radius; [b] using the mean air concentrations at each radius; [c] using the maximum air concentrations at each radius. [d] there were 1 wells with the largest air concentrations at the radius of 1,600 m, and the air concentrations at other radius on those wells were zeros. Since the occupational exposures and associated risks were investigated in this study, the air concentrations at the radius of 1,600 m were not considered.

Table A-36. Air concentrations for each chemical related to hydraulic fracturing (μg m^{-3}) based on the models used are listed.

Substances (CASRN)	Observation data		Modeling data				
	Ref.1 [a]	Ref. 2 [b]	This study [c]	Ref. 3 [d]	This study [e]	This study [f]	This study [g]
	NA	NA	AP-42 Chapter 7	Stagnant two-film model (Equation A-39)	AP-42 Chapter 4.3	AP-42 Chapter 4.3	AP-42 Chapter 7
	NA	NA	AERMOD	Box model (Equation A-40)	AERMOD	AERMOD	AERMOD
Ethylbenzene (100-41-4)	NA (3.04-3.04)	0.17(0.056,8.1) 0.77(0.25, 230)	5.06e-04 (2.70e-08,8.74e-02)	0.74 (0.0038-7.6)	6.60e-01 (3.37e-03, 6.73e+00)	5.13e-01 (2.62e-03, 5.24e+00)	4.37e-01 (7.50e-02,1.71e+01)
Styrene (100-42-5)	NA (3.83-3.83)	0.15(0.017,3.4) 0.13(0.23, 5.9)	NA	0.75 (0.0047-7.7)	6.72e-01 (4.25e-03, 6.85e+00)	5.23e-01 (3.31e-03, 5.33e+00)	NA
Benzaldehyde (100-52-7)	0.43 (0.43-0.43)	NA	NA	NA	NA	NA	NA
n-butane (106-97-8)	7.60 (1.90-33.27)	NA	NA	NA	NA	NA	NA
1,3-butadiene (106-99-0)	NA	0.11(0.025,0.15) 0.11(0.068, 0.17)	NA	NA	NA	NA	NA
1,2-dichloroethane (107-06-2)	NA	NA	NA	0.94 (0.0055-9.2)	7.96e-01 (4.68e-03, 7.80e+00)	6.19e-01 (3.64e-03, 6.07e+00)	NA
2-methylpentane (107-83-5)	2.82 (1.06-7.75)	NA	NA	NA	NA	NA	NA
m/p-xylenes (108-38-3/106-42-3)	1.74 (0.87-3.04)	0.87(0.16,9.9) 7.8(2.0, 880)	NA	NA	NA	NA	NA
1,3,5-trimethylbenzene (108-67-8)	NA	0.12(0.024,1.2) 1.3(0.33, 78)	1.96e-06 (4.62e-08,3.12e-03)	NA	NA	NA	2.18e-03 (7.51e-04,5.95e-02)
Methylcyclohexane (108-87-2)	3.61 (1.20-12.44)	3.7(0.15,24) 14(3.1, 720)	NA	NA	NA	NA	NA
Toluene (108-88-3)	4.52 (1.51-16.20)	1.8(0.11,79) 7.8(2.7, 320)	5.50e-05 (1.23e-07,4.56e+00)	4.04 (0.0047-37)	3.48e+00 (4.06e-03, 3.19e+01)	2.71e+00 (3.16e-03, 2.48e+01)	4.87e-02 (3.22e-03,1.51e+01)
n-pentane (109-66-0)	4.42 (1.18-16.52)	9.1(0.23,62) 11(3.9, 550)	NA	NA	NA	NA	NA
Tetrahydrofuran (109-99-9)	NA (6.19-6.19)	NA	NA	NA	NA	NA	NA
n-hexane (110-54-3)	3.17 (1.06-10.57)	4.0(0.13,25) 7.7(1.7, 255)	NA	NA	NA	NA	NA
Cyclohexane (110-82-7)	2.06 (1.03-5.51)	2.1(0.11,105) 5.3(2.21, 200)	NA	NA	NA	NA	NA

Table A-36. Air concentrations for each chemical related to hydraulic fracturing (μg m^{-3}) based on the models used are listed. (Continued)

Substances (CASRN)	Observation data		Modeling data				
	Ref.1 [a]	Ref. 2 [b]	This study [c]	Ref. 3 [d]	This study [e]	This study [f]	This study [g]
	NA	NA	AP-42 Chapter 7	Stagnant two-film model (Equation A-39)	AP-42 Chapter 4.3	AP-42 Chapter 4.3	AP-42 Chapter 7
	NA	NA	AERMOD	Box model (Equation A-40)	AERMOD	AERMOD	AERMOD
n-nonane (111-84-2)	1.05 (1.05-1.57)	0.44(0.064,3.1) 3.6(1.2, 300)	NA	NA	NA	NA	NA
n-dodecane (112-40-3)	NA (2.09-2.09)	NA	3.69e-05 (6.89e-09,2.10e-02)	NA	NA	NA	1.99e-02 (5.76e-03,8.90e-01)
Propylene (115-07-1)	NA	0.34(0.11,2.5) 0.41(0.16, 1.9)	NA	NA	NA	NA	NA
1,2,4-trichlorobenzene (120-82-1)	NA	NA	NA	0.53 (0.0034-6.8)	4.97e-01 (3.18e-03, 6.37e+00)	3.86e-01 (2.48e-03, 4.95e+00)	NA
Propionaldehyde (123-38-6)	0.24 (0.24-0.47)	NA	NA	NA	NA	NA	NA
Crotonaldehyde (123-73-9)	3.73 (0.29-8.60)	NA	5.57e-05 (9.77e-06,6.04e-03)	NA	NA	NA	5.14e-02 (2.74e-02,1.19e+00)
xylenes(total) (1330-20-7)	NA	NA	9.01e-06 (1.63e-08,2.95e-01)	5.9 (0.039-89)	5.25e+00 (3.50e-02, 7.94e+01)	4.08e+00 (2.72e-02, 6.18e+01)	6.41e-03 (1.42e-03,2.32e+01)
n-heptane (142-82-5)	2.46 (1.23-5.74)	NA	NA	NA	NA	NA	NA
benzo(g,h,i)perylene (191-24-2)	2.49 (1.02-5.08)	NA	NA	NA	NA	NA	NA
indeno(1,2,3-cd)pyrene (193-39-5)	2.03 (1.02-5.54)	NA	NA	NA	NA	NA	NA
benzo(b)fluoranthene (205-99-2)	2.06 (1.34-2.68)	NA	NA	NA	NA	NA	NA
benzo(k)fluoranthene (207-08-9)	1.86 (1.34-2.58)	NA	NA	NA	NA	NA	NA
Acenaphthylene (208-96-8)	NA (1.24-1.24)	NA	NA	NA	NA	NA	NA
Acetylene (2122-48-7)	1.43 (0.92-2.46)	NA	NA	NA	NA	NA	NA
Chrysene (218-01-9)	NA (1.12-1.49)	NA	NA	NA	NA	NA	NA
Cyclopentane (287-92-3)	NA (1.15-1.15)	NA	NA	NA	NA	NA	NA

Table A-36. Air concentrations for each chemical related to hydraulic fracturing (μg m^{-3}) based on the models used are listed. (Continued)

Substances (CASRN)	Observation data		Modeling data				
	Ref.1 [a]	Ref. 2 [b]	This study [c]	Ref. 3 [d]	This study [e]	This study [f]	This study [g]
	NA	NA	AP-42 Chapter 7	Stagnant two-film model (Equation A-39)	AP-42 Chapter 4.3	AP-42 Chapter 4.3	AP-42 Chapter 7
	NA	NA	AERMOD	Box model (Equation A-40)	AERMOD	AERMOD	AERMOD
Formaldehyde (50-00-0)	1.23 (0.37-2.95)	NA	7.09e-03 (8.22e-06,2.05e+03)	NA	NA	NA	4.54e+00 (1.44e+00,6.44e+02)
benzo(a)pyrene (50-32-8)	2.17 (1.34-3.71)	NA	NA	NA	NA	NA	NA
1,2,3-trimethylbenzene (526-73-8)	NA	0.11(0.022,0.85) 0.84(0.055, 12)	2.26e-07 (4.52e-09,9.09e-04)	NA	NA	NA	2.15e-04 (7.62e-05,9.95e-02)
dibenzo(a,h)anthracene (53-70-3)	2.28 (1.25-5.80)	NA	NA	NA	NA	NA	NA
Carbontetrachloride (56-23-5)	NA	NA	NA	0.83 (0.0043-8.6)	7.04e-01 (3.67e-03, 7.34e+00)	5.48e-01 (2.85e-03, 5.71e+00)	NA
benzo(a)anthracene (56-55-3)	NA (1.21-1.49)	NA	NA	NA	NA	NA	NA
3-methylhexane (589-34-4)	2.05 (1.23-4.51)	NA	NA	NA	NA	NA	NA
3-methylheptane (589-81-1)	NA (1.40-1.40)	NA	NA	NA	NA	NA	NA
2-methylhexane (591-76-4)	1.64 (0.82-2.87)	NA	NA	NA	NA	NA	NA
2-methylheptane (592-27-8)	1.40 (1.40-1.40)	NA	NA	NA	NA	NA	NA
Ethanol (64-17-5)	21.47 (6.03-36.54)	NA	1.40e-02 (0.00e+00,1.33e+02)	NA	NA	NA	7.93e+00 (1.77e+00,3.45e+02)
Hexaldehyde (66-25-1)	0.41 (0.41-0.82)	NA	NA	NA	NA	NA	NA
Methanol (67-56-1)	23.97 (15.85-40.08)	NA	4.61e-02 (1.01e-08,1.46e+03)	NA	NA	NA	3.17e+01 (7.33e+00,6.34e+02)
Acetone (67-64-1)	22.56 (8.07-67.20)	NA	2.00e-01 (3.41e-05,3.95e+01)	NA	NA	NA	4.38e+01 (9.81e+00,5.86e+02)
Benzene (71-43-2)	1.60 (0.96-3.51)	0.95(0.096,14) 2.6(0.94, 69)	2.43e-02 (4.03e-03,5.99e-02)	2.3 (0.0095-26)	1.94e+00 (7.97e-03, 2.19e+01)	1.51e+00 (6.20e-03, 1.70e+01)	2.12e+01 (8.66e+00,5.58e+01)
1,1,1-trichloroethane (71-55-6)	NA	NA	NA	0.81 (0.0043-8.6)	6.85e-01 (3.65e-03, 7.29e+00)	5.33e-01 (2.84e-03, 5.67e+00)	NA

Table A-36. Air concentrations for each chemical related to hydraulic fracturing (μg m^{-3}) based on the models used are listed. (Continued)

Substances (CASRN)	Observation data		Modeling data				
	Ref.1 [a]	Ref. 2 [b]	This study [c]	Ref. 3 [d]	This study [e]	This study [f]	This study [g]
	NA	NA	AP-42 Chapter 7	Stagnant two-film model (Equation A-39)	AP-42 Chapter 4.3	AP-42 Chapter 4.3	AP-42 Chapter 7
	NA	NA	AERMOD	Box model (Equation A-40)	AERMOD	AERMOD	AERMOD
Methane (74-82-8)	1621.64 (1049.22-3606.70)	NA	NA	NA	NA	NA	NA
Ethane (74-84-0)	30.00 (4.43-145.06)	NA	NA	NA	NA	NA	NA
Ethylene (74-85-1)	1.38 (0.92-2.06)	NA	NA	NA	NA	NA	NA
Propane (74-98-6)	16.77 (1.98-84.20)	NA	NA	NA	NA	NA	NA
Vinylchloride (75-01-4)	NA	NA	NA	1.8 (0.12-12)	1.35e+00 (9.10e-02, 9.10e+00)	1.05e+00 (7.08e-02, 7.08e+00)	NA
Acetaldehyde (75-07-0)	1.08 (0.54-3.24)	NA	3.58e-03 (1.48e-06,7.41e+00)	NA	NA	NA	1.50e+00 (6.49e-01,4.53e+01)
Methylenechloride (75-09-2)	715.97 (9.37-6006.91)	NA	4.97e-04 (4.61e-04,1.21e-03)	NA	NA	NA	4.13e-01 (4.09e-01,8.27e-01)
Isobutene (75-28-5)	6.89 (1.43-32.08)	NA	NA	NA	NA	NA	NA
Isopentane (78-78-4)	5.31 (1.18-21.53)	NA	NA	NA	NA	NA	NA
Isoprene (78-79-5)	1.67 (1.11-1.95)	NA	NA	NA	NA	NA	NA
Methacrolein (78-85-3)	0.29 (0.29-0.29)	NA	NA	NA	NA	NA	NA
1,2-dichloropropane (78-87-5)	NA	NA	NA	0.79 (0.0042-8.4)	6.80e-01 (3.62e-03, 7.23e+00)	5.29e-01 (2.81e-03, 5.63e+00)	NA
2-butanone(mek) (78-93-3)	10.02 (6.78-15.04)	NA	NA	NA	NA	NA	NA
mek&butyraldehyde (78-93-3/123-72-8)	0.59 (0.00-1.18)	NA	NA	NA	NA	NA	NA
1,1,2-trichloroethane (79-00-5)	NA	NA	NA	0.76 (0.00402-8.04)	6.75e-01 (3.59e-03, 7.18e+00)	5.25e-01 (2.79e-03, 5.59e+00)	NA
2,3-dimethylbutane (79-29-8)	1.41 (1.41-1.76)	NA	NA	NA	NA	NA	NA

Table A-36. Air concentrations for each chemical related to hydraulic fracturing (μg m^{-3}) based on the models used are listed. (Continued)

Substances (CASRN)	Observation data		Modeling data				
	Ref.1 [a]	Ref. 2 [b]	This study [c]	Ref. 3 [d]	This study [e]	This study [f]	This study [g]
	NA	NA	AP-42 Chapter 7	Stagnant two-film model (Equation A-39)	AP-42 Chapter 4.3	AP-42 Chapter 4.3	AP-42 Chapter 7
	NA	NA	AERMOD	Box model (Equation A-40)	AERMOD	AERMOD	AERMOD
Phenanthrene (85-01-8)	2.62 (1.53-4.44)	NA	NA	NA	NA	NA	NA
Fluorine (86-73-7)	1.36 (1.02-2.17)	NA	NA	NA	NA	NA	NA
Naphthalene (91-20-3)	21.96 (5.92-44.28)	NA	9.04e-07 (2.66e-11,1.88e-02)	NA	NA	NA	4.76e-04 (7.48e-05,3.27e-02)
o-xylene (95-47-6)	NA	0.22(0.064,3.6) 1.2(0.38, 190)	NA	NA	NA	NA	NA
1,2,4-trimethylbenzene (95-63-6)	NA (0.98-1.47)	0.18(0.063,3.1) 1.7(0.44, 83)	2.80e-05 (1.82e-09,1.20e-01)	NA	NA	NA	1.39e-02 (3.32e-03,3.98e-01)
3-methylpentane (96-14-0)	2.82 (1.06-7.05)	NA	NA	NA	NA	NA	NA
Methylcyclopentane (96-37-7)	2.06 (1.03-4.47)	NA	NA	NA	NA	NA	NA
Isopropylbenzene (98-82-8)	NA (1.47-1.47)	0.15(0.020,0.33) 0.33(0.0, 4.8)	5.43e-07 (1.08e-08,1.12e-02)	NA	NA	NA	6.03e-04 (2.05e-04,2.62e-02)

[a] values are presented as mean (min - max). Air samples were collected in Garfield County, Colorado from July, 2010 to October, and there were 130 natural gas wells and 2 vertical drilling well pads within 1 mile away from the sample site. Ref. 1: Colborn et al. (2014).

[b] values are presented as median (min - max) in natural gas development area sample and median (min - max) in well completion sample. Ref. 2: McKenzie et al. (2012).

[c] values are shown as median (min - max) in the average air concentrations at the distance of 180 m among all the wells adding the specific chemical.

[d] air concentrations by emissions from open flowback pits are shown as mean (2.5th percentile - 97.5th percentile). Ref. 3: Bloomdahl et al. (2014).

[e] emission data from the open flowback pits were calculated by equations in the AP- 42 Chapter 4.3 under the same situations described in Bloomdahl et al. (2014).Meteorological data used in the AERMOD was taken from Bloomdahl et al. (2014) (Note 1). The highest air concentrations from 5 to 180 m under the median, 2.5th percentile, and 97.5th percentile emissions were reported.

[f] being different with [e], meteorological data in 4,270 (out of 70,203) hydraulic fracturing wells located in the Marcellus Shale Play were used for the AERMOD. Under the median, 2.5th percentile, and 97.5th percentile emissions, the median values in the highest air concentrations from 5 to 180 m at each well were reported.

[g] the highest air concentrations from 5 to 180 m at each well caused by emissions from chemical storage tanks are presented as median (2.5th percentile – 97.5th percentile).

NA: not available

Note 1: The obtained maximum air concentration was 17.38 μg m^{-3} by AERSCREEN (the screen version of AERMOD) with the input parameters: 1) areacirc parameters: areacirc emission rate (6.35×10^{-3} g s^{-1}), areacirc height (0 m), areacirc radius (21.50 m), vertical dimension (2.43 m), rural, flagpole receptor height (1.67 m), initial probe distance (200 m); 2) without building downwash; 3) MAKEMET meteorology parameters: min/max temperature (298.0/298.2 K), minimum wind speed (4.0 m s^{-1}), anemometer height (10.0 m), surface characteristics input (AERMET SEASONAL TABLES), dominant surface profile (Grassland), dominant climate type (Average Moisture).

Table A-37. Inhalation risks caused by the open flowback pits and the chemical storage tanks are listed based on the distance from the emissions sources.

Distances (m)	Risks from the open flowback pits [a]								Risks from the chemical storage tanks							
	Caused by the median values in the average air concentrations with the median emissions				Caused by the median values in the highest air concentrations with the 97.5th percentile emissions				Caused by the median values in the average air concentrations				Caused by the 97.5th percentile values in the highest air concentrations			
	Non-Cancer		Cancer		Non-Cancer		Cancer		Non-Cancer		Cancer		Non-Cancer		Cancer	
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic
5	0.12	0.01	1.81E-05	1.33E-06	1.83	0.13	2.37E-04	1.74E-05	0.00	0.00	0.00E+00	0.00E+00	1.35	0.10	1.04E-03	7.59E-05
10	0.11	0.01	1.68E-05	1.23E-06	2.17	0.16	2.81E-04	2.06E-05	0.01	0.00	5.86E-07	4.29E-08	1.92	0.14	1.56E-03	1.14E-04
20	0.09	0.01	1.40E-05	1.02E-06	2.72	0.20	3.52E-04	2.58E-05	0.00	0.00	3.94E-07	2.88E-08	1.35	0.10	1.01E-03	7.40E-05
50	0.03	0.00	5.07E-06	3.71E-07	1.84	0.13	2.38E-04	1.74E-05	0.00	0.00	1.21E-07	8.88E-09	0.82	0.06	4.62E-04	3.38E-05
80	0.02	0.00	2.23E-06	1.63E-07	1.04	0.08	1.34E-04	9.83E-06	0.00	0.00	5.69E-08	4.16E-09	0.48	0.04	2.55E-04	1.86E-05
120	0.01	0.00	1.10E-06	8.02E-08	0.62	0.05	8.07E-05	5.90E-06	0.00	0.00	2.86E-08	2.09E-09	0.28	0.02	1.47E-04	1.07E-05
150	0.01	0.00	7.42E-07	5.43E-08	0.46	0.03	6.02E-05	4.40E-06	0.00	0.00	1.95E-08	1.43E-09	0.21	0.02	1.09E-04	7.99E-06
180	0.00	0.00	5.40E-07	3.95E-08	0.36	0.03	4.71E-05	3.45E-06	0.00	0.00	1.42E-08	1.04E-09	0.16	0.01	8.38E-05	6.13E-06

[a] Air concentrations were calculated by AERMOD with the meteorological data in 70,203 hydraulic fracturing wells obtained from the nearest observation stations. Emissions were calculated by the AP-42 Chapter 4.3 under the same situations descried in Bloomdahl et al. (2014).

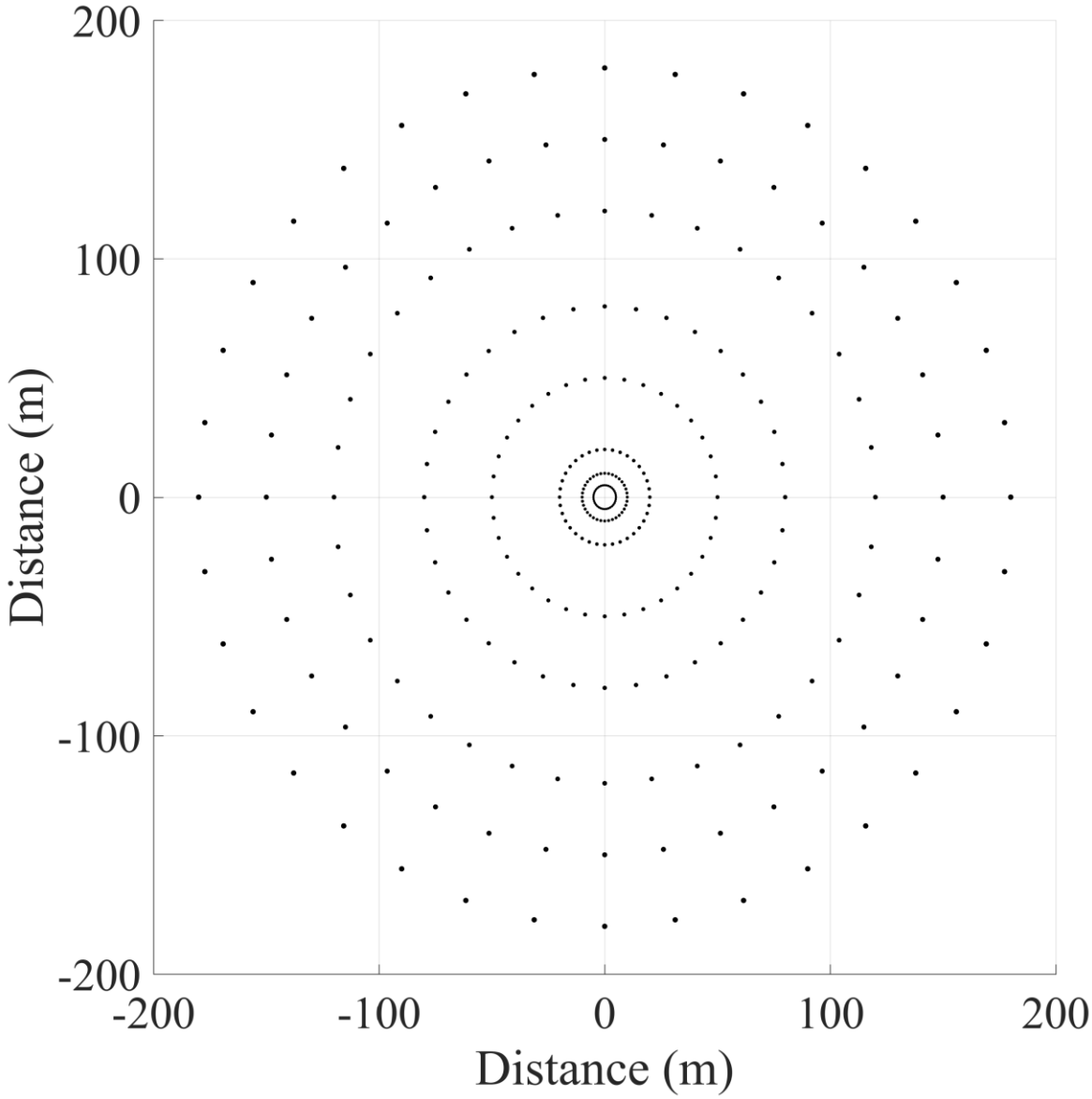

Figure A-21. Distribution of all the receptors at each well. Emission source is located at the center of eight circles which have the radius of 5, 10, 20, 50, 80, 120, and 180 meters. There were 36 receptors evenly distributed at each circle.

VITA

Huan Chen was born in Jiang Xi province in China on Sep 26th, 1984. He obtained his Bachelor of Engineering degree in Environmental Engineering from the Department of Environmental Science and Engineering at the Southwest Jiaotong university, Chengdu, China, which was founded in 1886 as the Imperial Chinese Railway College. After the graduation on July 2006, he passed the national entrance examination for postgraduates and entered the Department of Environmental Science and Engineering at the Peking University, Beijing, China, founded in 1898 and named the Imperial University of Peking at that time. He obtained a Master of Science degree in Environmental Engineering after three years. In 2013, he came to the United States and went to the Department of Civil and Environmental Engineering at the University of Tennessee, Knoxville (founded in 1794) for his Ph.D. degree in Civil Engineering after working for four years at Shenzhen, China. Due to the affections on the nature and ecosystem, his interested areas include environmental modeling, advanced oxidation processes, waste-to-energy, recycling and reuse, and risk assessments. His dissertation towards the Ph.D. degree is evaluating the inhaled occupational risk from the chemical storage tanks in hydraulic fracturing, which involves water usages for mixing chemical additives to make up the hydraulic fracturing fluids in hydraulic fracturing, chemical fate and transport between the aqueous and gas phases, chemical dispersions at the atmosphere, and inhalation risk assessments. Data mining, environmental modeling, and parallel computing were the technologies employed in his dissertation.

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June 3, 2016

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